

# Chemistry-climate interactions in the Goddard Institute for Space Studies general circulation model

## 1. Tropospheric chemistry model description and evaluation

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**Abstract.** A tropospheric chemistry model has been developed within the Goddard Institute for Space Studies general circulation model (GCM) to study interactions between chemistry and climate change. The model uses simplified chemistry based on CO-NO<sub>x</sub>-HO<sub>x</sub>-O<sub>x</sub>-CH<sub>4</sub> and also includes a parameterization for isoprene emissions, the most important non-methane hydrocarbon. The model reproduces observed annual cycles and mean distributions of key trace gases fairly well. It simulates preindustrial to present-day changes similar to those seen in other simulations. For example, the global tropospheric ozone burden increases 45%, within the 25% - 57% range of other studies. Annual average zonal mean surface ozone increases more than 125% at northern midlatitudes. Comparison between runs that allow calculated ozone to interact with the GCM and those that do not shows only minor ozone differences. The common usage of non-interactive ozone seems adequate to simulate ozone distributions. However, use of coupled chemistry does alter the tropospheric oxidation capacity, enlarging the preindustrial to present-day OH decrease by about 10% (-5.3% global annual average uncoupled, -5.9% coupled). Thus simulation of changes in oxidation capacity may be systematically biased (though a 10% difference is within the uncertainty). Global annual average radiative forcing from preindustrial to present-day ozone change is 0.32 W m<sup>-2</sup>. The forcing seems to increase by ~10% with coupled chemistry. Forcing greater than 0.8 W m<sup>-2</sup> is seen over the United States, the Mediterranean area, central Asia, and the Arctic, with values greater than 1.5 W m<sup>-2</sup> over parts of these areas during summer. Though there are local differences, the radiative forcing is overall in good agreement with other modeling studies in both magnitude and spatial distribution, demonstrating that the simplified chemistry is adequate for climate studies.

## 1. Introduction

The buildup of both greenhouse gases and ozone precursors in the Earth's atmosphere due to anthropogenic emissions is well documented [e.g., *International Panel on Climate Change (IPCC)*, 1996]. Since preindustrial times, carbon dioxide has increased by ~30%, methane by about 150%, and NO<sub>x</sub> is thought to have more than doubled. Just since the 1950s, carbon monoxide levels have increased by 50% at Northern Hemisphere midlatitudes. The direct radiative influence of the well-mixed greenhouse gases has been studied intensely and is now considered to be one of the lesser sources of uncertainty for recent climate change [e.g., *Hansen et al.*, 1998]. Induced changes in chemistry are much less clear. These changes have an indirect radiative effect by chemically altering the abundance of radiatively absorbing species such as ozone and methane.

The major chemical impacts of increasing emissions of greenhouse gases and ozone precursor gases such as nitrogen oxides (NO<sub>x</sub>) are to produce tropospheric ozone, and to alter tropospheric OH (which, along with ozone, largely governs the oxidation capacity of the troposphere). Ozone production requires NO<sub>2</sub> photolysis to create atomic oxygen, which then combines with molecular oxygen to form ozone, and hydrocarbons or carbon monoxide to turn OH into HO<sub>2</sub>, which is necessary to allow the regeneration of NO<sub>2</sub> from the photolysis product NO. As ozone precursor gases have increased, enhanced tropospheric ozone abundances have resulted. In Northern Hemisphere industrial areas, surface ozone has doubled since the 1930s, while the entire tropospheric ozone column has increased by 20% over Europe just in the 1980s. Recent work indicates that tropospheric ozone changes may have accounted for a radiative forcing of up to ~1 W m<sup>-2</sup>, which is roughly 30% of the total forcing due to greenhouse gases [*Portmann et al.*, 1997]. The amount of OH is reduced by the presence of greater levels of methane and carbon monoxide in the atmosphere, which alter the partitioning among hydrogen oxides (HO<sub>x</sub>), favoring HO<sub>2</sub> over OH. While these changes are partially offset by the effects of increased NO<sub>x</sub>, ozone, water vapor, and temperature, all of which tend to increase the abundance of OH, the net effect of changes over the past 150 years seems to have been a decrease in OH concentration. This reduction of the tropospheric oxidation

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capacity acts as an important climate feedback, since oxidation via OH is the primary removal mechanism for tropospheric methane and carbon monoxide.

It is therefore necessary to include future levels of ozone precursors along with atmospheric chemistry in order to simulate future abundances of the greenhouse gases methane and ozone. Given the enormous computation costs of running a large climate model with interactive chemistry, we have chosen to develop a simplified scheme based on current understanding of the most important chemical processes in the troposphere. The clear advantage of using a simplified chemistry scheme is that the rapid computational speed allows for longer simulations to be run, permitting the model's variability to be accurately assessed, and for numerous sensitivity experiments to be performed, which is crucial to unraveling the complex interlinkages involved in chemistry-climate coupling. We present here detailed documentation of our simplified tropospheric chemistry model. Its performance is then evaluated based on comparison with observations for the present day, and its sensitivity to a commonly modeled perturbation is compared with other models. The model has been applied to sensitivity studies of chemistry and climate interactions in a follow-up paper (J. L. Grenfell et al., Chemistry-climate interactions in the GISS GCM, 2, New insights into modeling the preindustrial atmosphere, submitted to *Journal of Geophysical Research*, 2000) (hereinafter referred to as part 2), and has been applied to a study of upper tropospheric nitrogen oxides and ozone [Grewe et al., 2001].

## 2. Model Description

### 2.1. Chemistry

It is computationally very expensive to model the full range of chemical reactions in the troposphere in a general circulation model (GCM) suitable for climate studies. Therefore we have chosen to use a subset of molecules and include only the photochemical reactions that involve those chosen species. It is now accepted that the abundance of ozone is most often limited by the availability of  $\text{NO}_x$ , rather than the hydrocarbons which are also ozone precursors [e.g., Trainer et al., 1993]. Therefore we have not included an explicit representation of non-methane hydrocarbons (NMHCs) in our reduced chemistry scheme. We do, however, include equivalent carbon monoxide emissions from isoprene, which is thought to be the most important contribution of NMHCs [Wang et al., 1998c; Horowitz et al., 1998].

The simplified chemistry scheme is based on  $\text{CH}_4$ ,  $\text{CO}$ ,  $\text{NO}_x$  ( $\text{NO} + \text{NO}_2 + \text{NO}_3 + \text{HONO}$ ),  $\text{HO}_x$  ( $\text{OH}$ ,  $\text{HO}_2$ ), and  $\text{O}_x$  ( $\text{O} + \text{O}(^1\text{D}) + \text{O}_3$ ) chemistry. Methane is set to fixed values in the troposphere, with 1.80 parts per million by volume (ppmv) in the Northern Hemisphere and 1.70 ppmv in the Southern Hemisphere for the present-day simulations (early 1990s values). Use of the chemical family approach, whereby radical species in particular "families" (e.g., odd oxygen) are grouped together, and the reactions between family members are assumed to be rapid enough to maintain an equilibrium partitioning between individual family members at all times, yields a great computational time savings. We are then able to treat the family as a single species for transport. Combined with the reduced chemistry set, we are able to use relatively few chemical tracers. The number of online tracers is an important factor in these simulations, as they are transported by a quadratic upstream scheme [Prather, 1986], which is very accurate (saving second-order moments in all directions), but also very time consuming. Having few tracers allows the model to run much faster and is a further motivation to use simplified chemistry. Ten chemical species are transported in the model:

$\text{O}_x$ ,  $\text{NO}_x$ ,  $\text{H}_2\text{O}_2$ ,  $\text{H}_2\text{O}$ ,  $\text{CO}$ ,  $\text{HNO}_3$ ,  $\text{N}_2\text{O}_5$ ,  $\text{HO}_2\text{NO}_2$ ,  $\text{CH}_3\text{OOH}$ , and  $\text{HCHO}$ . This is a significant savings over transporting all 24 molecules used in the simulations. After combining the short-lived radicals into equilibrated families, we find that all the species have long enough lifetimes (except for  $\text{HO}_x$ , whose very short lifetime keeps it in equilibrium at all times) that we can use an extremely simple explicit scheme to calculate chemical changes, using a chemical time step of 1 hour. The chemistry scheme adds ~56% to the running time of the GCM, with 38% from chemistry and 18% from tracer transport.

The chemical scheme includes 52 reactions. Gas phase and heterogeneous chemical reactions are given in Table 1. Heterogeneous hydrolysis of  $\text{N}_2\text{O}_5$  into  $\text{HNO}_3$  takes place on sulfate aerosols, using the reaction rate coefficients given by Dentener and Crutzen [1993]. Sulfate surface areas are taken from an online calculation also performed with the Goddard Institute for Space Studies (GISS) GCM [Koch et al., 1999], assuming a monodispersed size distribution. This is not entirely self-consistent as meteorology, and therefore clouds, changes from run to run, which would affect sulfate. In the future we will attempt to couple the simulations of ozone and sulfate chemistry. Both may be affected, as the sulfate simulation relies on fixed fields of radical species, much as the ozone simulation presented here relies on a fixed sulfate distribution. The heterogeneous reaction on sulfate is critical to the model's ability to properly simulate the partitioning of nitrogen species in the dark.

Photolysis rates are calculated with Fast-J, a scheme which uses only seven wavelength intervals yet deviates only slightly from a full line-by-line calculation (M. Prather, personal communication, 1999) and compares well with other photolysis schemes [Olson et al., 1997]. The photolysis reactions included in the model are listed in Table 2. Photolysis calculations are performed every 2 hours, giving us a fairly realistic diurnal simulation.

### 2.2. Sources and Sinks

Emission inventories of  $\text{NO}_x$  and  $\text{CO}$  have been compiled for the  $4 \times 5$  degree latitude by longitude grid used in this model. The use of detailed  $\text{NO}_x$  and  $\text{CO}$  emissions is critical since emissions vary widely with location. Nitrogen oxide sources are quite similar to those specified for the NASA Subsonic Assessment aircraft project, consisting of annual emissions from fossil fuel burning (22.6 Tg N yr<sup>-1</sup>) taken from the Global Emission Inventory Activity (GEIA) data set [Benkovitz et al., 1996], and monthly emissions from biomass burning (5.3 Tg N yr<sup>-1</sup>) from GEIA [Laursen et al., 1992], soils (5.9 Tg N yr<sup>-1</sup>) from Müller [1992], and aircraft (0.6 Tg N yr<sup>-1</sup>) from Baughcum et al. [1996], as given by Friedl [1997, and references therein] (Table 3).  $\text{CO}$  emissions from energy use (520 Tg CO yr<sup>-1</sup>) and from biomass burning (510 Tg CO yr<sup>-1</sup>) are as given by Wang et al. [1998a]. An additional  $\text{CO}$  source is the conversion of isoprene emissions (yielding 145 Tg CO yr<sup>-1</sup>), based on 590 Tg C yr<sup>-1</sup> emission in isoprene as calculated by Wang et al. [1998a] as a function of temperature, vegetation type, leaf area index, and solar radiation, and then assuming an 11% conversion to carbon monoxide per molecule carbon (this value is quite uncertain and may depend upon various factors including  $\text{NO}_x$  abundances) [see, e.g., Horowitz et al., 1998]. Emissions are from data sets for as close to 1990 as available, in practice ranging from 1985 to 1992. This period corresponds well with the data used to evaluate the model, which was predominantly taken during the 1980s and the early 1990s.

To model nitrogen oxides produced by lightning, the GISS convection scheme is first used to derive both the total lightning, and the cloud-to-ground lightning frequencies

**Table 1.** Chemical Reactions Included in the Model<sup>a</sup>

Bimolecular Reaction		A Factor	Activation Temperature		
(1)	$\text{OH} + \text{HO}_2 \rightarrow \text{H}_2\text{O} + \text{O}_2$	4.80E-11	-250.		
(2)	$\text{OH} + \text{O}_3 \rightarrow \text{HO}_2 + \text{O}_2$	1.60E-12	940.		
(3)	$\text{OH} + \text{OH} \rightarrow \text{H}_2\text{O} + \text{O}$	4.20E-12	240.		
(4)	$\text{HO}_2 + \text{O}_3 \rightarrow \text{OH} + \text{O}_2$	1.10E-14	500.		
(5)	$\text{O}_3 + \text{NO} \rightarrow \text{NO}_2 + \text{O}_2$	2.00E-12	1400.		
(6)	$\text{HO}_2 + \text{NO} \rightarrow \text{OH} + \text{NO}_2$	3.50E-12	-250.		
(7)	$\text{NO}_2 + \text{O}_3 \rightarrow \text{NO}_3 + \text{O}_2$	1.20E-13	2450.		
(8)	$\text{O}(^1D) + \text{O}_2 \rightarrow \text{O} + \text{O}_2$	3.20E-11	-70.		
(9)	$\text{O}(^1D) + \text{M} \rightarrow \text{O} + \text{M}$	1.30E-11	-110.		
(10)	$\text{O}(^1D) + \text{H}_2\text{O} \rightarrow \text{OH} + \text{OH}$	2.20E-10	0.		
(11)	$\text{O}(^1D) + \text{CH}_4 \rightarrow \text{OH} + \text{CH}_3\text{O}_2$	1.50E-10	0.		
(12)	$\text{CH}_4 + \text{OH} \rightarrow \text{H}_2\text{O} + \text{CH}_3\text{O}_2$	2.45E-12	1775.		
(13)	$\text{CO} + \text{OH} \rightarrow \text{HO}_2 + \text{CO}_2$	1.50E-13	0.		
(14)	$\text{OH} + \text{H}_2\text{O}_2 \rightarrow \text{H}_2\text{O} + \text{HO}_2$	2.90E-12	160.		
(15)	$\text{HO}_2 + \text{HO}_2 \rightarrow \text{H}_2\text{O}_2 + \text{O}_2$	2.30E-13	-600.		
(16)	$\text{OH} + \text{HNO}_3 \rightarrow \text{H}_2\text{O} + \text{NO}_3$	7.20E-15	-785.		
(17)	$\text{NO}_3 + \text{NO} \rightarrow \text{NO}_2 + \text{NO}_2$	1.50E-11	-170.		
(18)	$\text{OH} + \text{HO}_2\text{NO}_2 \rightarrow \text{H}_2\text{O} + \text{NO}_2$	1.30E-12	-380.		
(19)	$\text{H}_2 + \text{OH} \rightarrow \text{HO}_2 + \text{H}_2\text{O}$	5.50E-12	2000.		
(20)	$\text{CH}_3\text{O}_2 + \text{NO} + \text{HO}_2 \rightarrow \text{HCHO} + \text{NO}_2$	3.00E-12	-280.		
(21)	$\text{HCHO} + \text{OH} + \text{H}_2\text{O} \rightarrow \text{HO}_2 + \text{CO}$	1.00E-11	0.		
(22)	$\text{CH}_3\text{O}_2 + \text{HO}_2 \rightarrow \text{CH}_3\text{OOH} + \text{O}_2$	3.80E-13	-800.		
(23)	$\text{CH}_3\text{OOH} + \text{OH} \rightarrow \text{CH}_3\text{O}_2 + \text{H}_2\text{O}$	3.80E-12	-200.		
(24)	$\text{NO}_2 + \text{NO}_3 \rightarrow \text{NO} + \text{NO}_2 + \text{O}_2$	4.50E-14	1260.		
(25)	$\text{NO}_3 + \text{NO}_3 \rightarrow \text{NO}_2 + \text{NO}_2 + \text{O}_2$	8.50E-13	2450.		
(26)	$\text{OH} + \text{HONO} \rightarrow \text{H}_2\text{O} + \text{NO}_2$	1.80E-11	390.		
(27)	$\text{CH}_3\text{O}_2 + \text{CH}_3\text{O}_2 \rightarrow \text{HCHO} + \text{HCHO}$	2.25E-13	-190.		
(28)	$\text{NO}_3 + \text{HCHO} \rightarrow \text{HNO}_3 + \text{CO} + \text{HO}_2$	5.80E-16	1900.		
Monomolecular Breakup Reaction (Rates for Equilibrium Constants)		A Factor	Temperature Dependence		
(29)	$\text{HO}_2\text{NO}_2 + \text{M} \rightarrow \text{HO}_2 + \text{NO}_2$	2.10E-27	10900.		
(30)	$\text{N}_2\text{O}_5 + \text{M} \rightarrow \text{NO}_3 + \text{NO}_2$	2.70E-27	11000.		
Termolecular Reactions		$k_0$	$n$	$k_\infty$	$m$
(31)	$\text{O} + \text{O}_2 + \text{M} \rightarrow \text{O}_3 + \text{M}$	6.00E-34	2.3	0.00E-00	0.0
(32)	$\text{NO} + \text{O} + \text{M} \rightarrow \text{NO}_2 + \text{M}$	9.00E-32	1.5	3.00E-11	0.0
(33)	$\text{OH} + \text{OH} + \text{M} \rightarrow \text{H}_2\text{O}_2 + \text{M}$	6.20E-31	1.0	2.60E-11	0.0
(34)	$\text{OH} + \text{NO}_2 + \text{M} \rightarrow \text{HNO}_3 + \text{M}$	2.50E-30	4.4	1.60E-11	1.7
(35)	$\text{HO}_2 + \text{NO}_2 + \text{M} \rightarrow \text{HO}_2\text{NO}_2 + \text{M}$	1.80E-31	3.2	4.70E-12	1.4
(36)	$\text{NO}_3 + \text{NO}_2 + \text{M} \rightarrow \text{N}_2\text{O}_5 + \text{M}$	2.20E-30	3.9	1.50E-12	0.7
(37)	$\text{OH} + \text{NO} + \text{M} \rightarrow \text{HONO} + \text{M}$	7.00E-31	2.6	3.60E-11	0.1
Heterogeneous Reactions					
(38)	$\text{N}_2\text{O}_5 + \text{H}_2\text{O} \rightarrow 2 \text{HNO}_3$				

<sup>a</sup>Reaction rates for bimolecular reactions are given by  $A \exp((-E/R)(1/T))$ , where  $A$  is the Arrhenius  $A$  factor,  $E/R$  is the activation temperature of the reaction, and  $T$  is the temperature. For monomolecular reactions, the equilibrium constant is given by  $A \exp(B/T)$ , where  $A$  is again the  $A$  factor, and  $B$  is the temperature dependence of the reaction. For termolecular reactions, rates are calculated as a function of the high- and low-pressure reactions rates, given by  $k_{\infty}(T/300)^{-m}$  and  $k_0(T/300)^{-n}$ , respectively, where  $T$  is temperature. In all the above reactions,  $M$  is any body that can serve to carry away excess energy. Reaction (9) is multiplied by 0.72 to include only quenching reactions on molecular nitrogen, since reaction (8) accounts for those on oxygen molecules. Reactions (11) and (12) assume an instantaneous reaction of the methyl radical with oxygen to form CH<sub>3</sub>O<sub>2</sub>. Reactions (13), (15), and (16) include additional dependencies on pressure, pressure and water vapor, and pressure and temperature, respectively. Reaction (27) is multiplied by 0.9 to account for the yield of these products and includes a 33% yield of two HO<sub>2</sub> molecules. Reaction (28) is approximate.

<sup>b</sup>Read 4.80E-11 as 4.80 × 10<sup>-11</sup>.

interactively in each grid box and at each time step [Price *et al.*, 1997]. Then the production rate of NO<sub>x</sub> from lightning is used to derive the NO<sub>x</sub> produced, including a “C-shaped” vertical distribution of the lightning produced NO<sub>x</sub> [Pickering *et al.*, 1998]. Based on a comparison with the global lightning data set recently produced at NASA Marshall Space Flight Center [Boccippio *et al.*, 1998; W. Koshak, personal communication, 2000], we revised our original parameterization of the lightning flash frequency to allow cloud overshooting events during very strong convective activity, primarily at Northern Hemisphere mid-latitudes. In practice, this allows lightning to be generated one level above the nominal cloud top height. The model now gives more lightning at midlatitudes, improving

the overall simulation of the global lightning frequency field (see section 3.3).

Chemistry is only applied in the troposphere in this model (the lowest seven layers, up to ~140 mbar). Stratospheric sources for ozone and NO<sub>x</sub> are included. For ozone we keep stratospheric amounts at the observed, seasonally varying levels used in the standard GISS model [Hansen *et al.*, 1996] and then allow the model to transport ozone into the troposphere based on the existing gradients at each time step. NO<sub>x</sub> in the stratosphere is defined as a fraction of the ozone. This gives the basic structure of the observed NO<sub>x</sub> distribution, with larger values at higher latitudes and smaller values in the tropics due to the Brewer-Dobson circulation. The result is a

**Table 2.** Photolysis Reactions Included in the Model

Reaction
(1) $\text{NO}_2 \rightarrow \text{NO} + \text{O}$
(2) $\text{O}_3 \rightarrow \text{O(1D)} + \text{O}_2$
(3) $\text{O}_3 \rightarrow \text{O} + \text{O}_2$
(4) $\text{H}_2\text{O}_2 \rightarrow \text{OH} + \text{OH}$
(5) $\text{NO}_3 \rightarrow \text{NO} + \text{O}_2$
(6) $\text{NO}_3 \rightarrow \text{NO}_2 + \text{O}$
(7) $\text{N}_2\text{O}_5 \rightarrow \text{NO}_3 + \text{NO}_2$
(8) $\text{HONO} \rightarrow \text{OH} + \text{NO}$
(9) $\text{HNO}_3 \rightarrow \text{OH} + \text{NO}_2$
(10) $\text{HO}_2\text{NO}_2 \rightarrow \text{HO}_2 + \text{NO}_2$
(11) $\text{HO}_2\text{NO}_2 \rightarrow \text{OH} + \text{NO}_3$
(12) $\text{HCHO} \rightarrow \text{CO} + \text{H}_2$
(13) $\text{HCHO} \rightarrow \text{CO} + \text{HO}_2$
(14) $\text{CH}_3\text{OOH} \rightarrow \text{HCHO} + \text{HO}_2$

similar ratio in influx to the troposphere as both species have strong positive gradients with altitude around the tropopause. Though the coarse vertical resolution makes it difficult for the model to simulate cross-tropopause transport properly [Rind *et al.*, 1999], and we plan to improve this in the future, using internally calculated fluxes does give us an internally consistent formulation that produces reasonable tropospheric ozone fields, and can also respond to perturbations. To examine the importance of a possible overestimate of transport of stratospheric ozone and  $\text{NO}_x$  to the troposphere, a sensitivity study was performed in which the stratospheric amounts were reduced by two thirds.

Phase transformation and removal of soluble species is calculated using a wet deposition scheme as given by Koch *et al.* [1999]. Briefly, soluble gases can be removed into either moist convective plumes or large-scale clouds as derived from the GCM's internal cloud scheme [Del Genio and Yao, 1993]. During convection, all chemical species are transported along with the convective plumes, with scavenging of soluble species within and below cloud updrafts. In large-scale stratiform clouds, soluble gases are removed based on the fraction of the grid box over which precipitation is taking place. Washout of soluble species is calculated below precipitating clouds. In the case of either evaporation of precipitation before reaching the ground, or detrainment or evaporation from a convective updraft, the dissolved species are returned to the air.

Wet chemistry calculations take place in each grid box at each time step, including the coupling with the convection scheme's entraining and nonentraining plumes (which are based on the convective instability in the particular grid box at that time), so are entirely consistent with the contemporaneous model physics. The solubility of each gas is determined by an effective Henry's Law coefficient, assuming a pH of 4.5. Surface dry deposition is calculated using a resistance-in-series model [Wesely and Hicks, 1977] coupled to a global, seasonally varying vegetation data set as given by Chin *et al.* [1996]. Note that the leaf area indices are therefore not connected with the GCM's land-surface component. Aerodynamic resistances are based on the model's surface heat and momentum fluxes, as given by Koch *et al.* [1999].

### 2.3. Climate Model

The chemistry scheme has been installed directly into the latest version of the GISS climate model, II' (two-prime). This is a primitive equation model, run here with nine vertical layers, centered at 959, 894, 786, 634, 468, 321, 201, 103, and 26.5 mbar, and horizontal resolution of  $4 \times 5$  degrees

(latitude  $\times$  longitude). The bottom seven layers are terrain following sigma levels, while the top two are constant pressure surfaces. The GCM's physics time step is 1 hour, so that changes to tracer masses from transport and chemistry are both applied every hour. Several improvements have been made in recent years which will influence chemistry through their effects on transport and moisture content [Hansen *et al.*, 1983, 1996]. The boundary layer parameterization has been recently revised and now employs a finite modified Ekman layer with parameterizations for drag and mixing coefficients based on similarity theory, which impacts the vertical mixing of surface fluxes. Convection now includes entraining and nonentraining plumes, mass fluxes proportional to convective instability, explicit downdrafts, and the model contains a cloud liquid-water scheme, based on microphysical sources and sinks of cloud water, which carries both water and ice [Del Genio *et al.*, 1996]. The land surface parameterization has been greatly expanded and now explicitly calculates transpiration, infiltration, soil water flow and runoff, all of which impact both water vapor and latent heat release to the atmosphere.

The capability of the GCM to model the transport of trace species accurately has also been greatly improved. All the chemical tracers, along with heat and moisture, are now advected using a quadratic upstream scheme [Prather, 1986]. (Momentum advection uses a fourth-order scheme). Additionally, improvements were made to the boundary layer and convection schemes [Del Genio *et al.*, 1996]. Improvements to transport both within the boundary layer and across the boundary layer edge, along with convection, are especially important, since trace gas emissions at the Earth's surface come from discrete, spatially inhomogeneous sources. A prime example of the improvements can be seen in the interhemispheric exchange times of CFC-11 and  $^{85}\text{Kr}$ . In the earlier version of the model the exchange times were roughly a factor of 2 too long, whereas in the new version, the values are within 15–25% of observations [Rind and Lerner, 1996]. Improvements in the interhemispheric exchange time occurred because the alterations in both the boundary layer and convection schemes improved the tropical precipitation and wind fields. Interestingly, neither change by itself was overly effective, a result which illustrates the highly nonlinear nature of GCM interactions. The GISS GCM II' has been used previously for ozone [Mickley *et al.*, 1999] and sulfate [Koch *et al.*, 1999] simulations.

The use of water vapor as an online, chemically active tracer is another important feature of this model. Most chemical models assume that water vapor is constant since they do not have a detailed model of the hydrological cycle, while most climate models do not have any chemistry. Thus the interaction between water vapor and climate through chemistry has seldom been examined, although it is thought to be an important issue in climate modeling [IPCC, 1996].

Calculated ozone fields are used in the GCM's computation of radiative heating and fluxes which is performed every 5 hours. These fully interactive chemical constituent changes are

**Table 3.**  $\text{NO}_x$  Budget<sup>a</sup>

Source/Sink	Value
Fossil fuels	22.6
Soils	5.9
Biomass burning	5.3
Lightning	3.9
Aircraft	0.6
Stratosphere	0.2
Chemistry	-33.2
Dry deposition	-5.3

<sup>a</sup>Units are  $\text{Tg N yr}^{-1}$  - annual mean.

therefore able to affect the meteorology in the GCM. To explore the influence of this feedback, we have also performed simulations where this feedback was not allowed, in which case the model used a climatological ozone distribution in its radiation calculations. In addition to ozone, the GCM calculates radiative absorption and emission from water, CO<sub>2</sub>, N<sub>2</sub>O, chlorofluorocarbons and methane in the longwave, and CO<sub>2</sub>, NO<sub>2</sub> and O<sub>2</sub> in the shortwave [Hansen *et al.*, 1983]. Changes in tropospheric ozone play an important role in the radiative heating that drives tropospheric meteorology, through their absorption in the Huggins bands in the ultraviolet, the Chappuis bands in the visible, and the 9.6 micron and especially the 14 micron bands in the infrared [Shine *et al.*, 1995; van Dorland *et al.*, 1997].

The simplified chemistry scheme adds only about 38% to the running time of the GCM, plus an additional ~18% for the transport of the chemical tracers. It is therefore computationally rapid enough that the GCM can be run with online chemistry for long-term climate simulations or for multiple runs to examine the sensitivity of the results to various changes. Although this model is certainly not as realistic as models containing more complete chemistry, it is able to reproduce the magnitude and variability (temporal, horizontal, and vertical) of important tropospheric trace gases on a global, three-dimensional basis, quite well, as detailed in section 3.

### 3. Evaluation of Present-Day Simulation

Model simulations of present-day conditions are taken from the last 9 years of 10-year runs (the model equilibrated during the first year), giving us good statistics on both the model's simulated mean values and its variability. These runs are evaluated by comparison with available tropospheric data sets. We focus primarily on ozone, due to its importance for climate modeling, and on its key precursors, CO and NO<sub>x</sub> (key in addition to methane, which is prescribed). Additionally, we examine hydrogen peroxide, which plays an important role in both hydrogen oxide and sulfate chemistry, a topic we plan to explore in the future.

#### 3.1. Ozone

Modeled annual cycles of ozone have been compared with the ozonesonde data climatology developed by Logan [1999]. We compare several levels where the modeled and observed pressures are quite close, using measurements at 200, 300, 500, 800, and 950 mbar compared with modeled values at 203, 323, 470, 787, and 959 mbar, respectively. We will refer to these levels by the more standard pressure values of the data. Standard deviations of the model and as reported for the observations are both shown. However, it is difficult to ascertain how comparable the reported variability is to the simulated variability. The number of years of data varies from station to station and is not always very large, yielding varied quality in the derived interannual variability. Additionally, sampling biases (e.g., not flying balloons in bad weather) could also reduce the reported variability. On the model side the large 4 × 5 degree grid box makes comparison with a single point quite difficult, and there could also be problems from numerical noise in the GCM's chemical or tracer transport schemes. We therefore concentrate on comparing the mean values and focus less on the variability.

Figure 1 shows the results of these comparisons for a sampling of sites covering a wide range of the globe in latitude. At the uppermost model level which includes chemistry, centered at 200 mbar, the model underestimates the

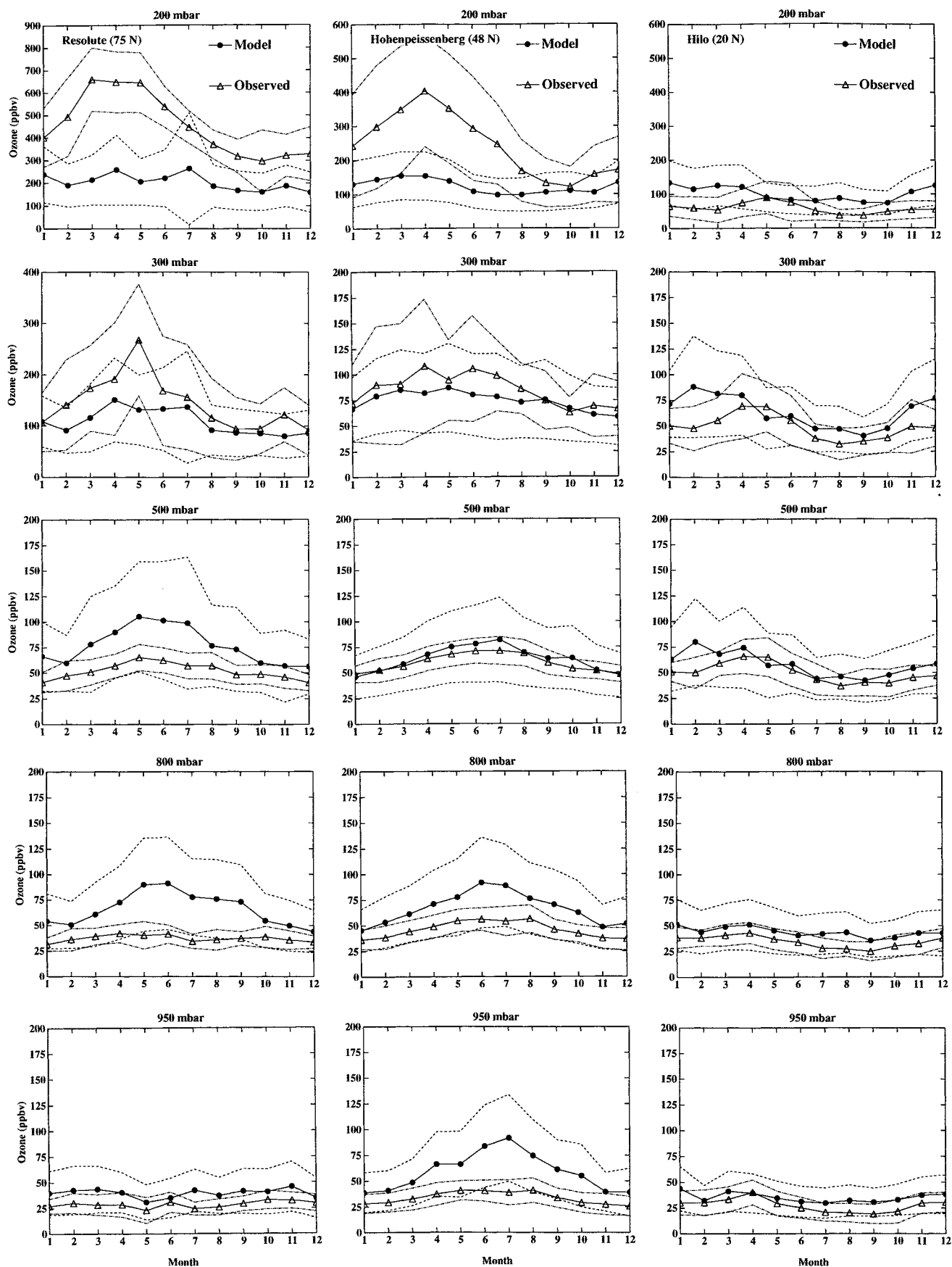
seasonal cycle at middle and high latitudes in both hemispheres, failing to capture the late winter/springtime ozone maximum seen in observations. The very large values measured at these levels tag the ozone as originating in the stratosphere (a commonly used threshold for identifying air as being stratospheric in origin is 150 parts per billion by volume (ppbv) (see, e.g., [Grewe *et al.*, 2001]). At polar latitudes, such as Resolute (75°N), this level is actually in the stratosphere during the late winter/spring season. This model is designed to simulate tropospheric chemistry only, so would not be expected to reproduce ozone values in stratospheric air. While a stratospheric ozone climatology is used in the model, the coarse vertical resolution of the model at these levels does not allow it to capture the seasonal motion of the tropopause accurately, nor to simulate stratosphere-troposphere exchange fully [Rind and Lerner, 1996]. The underestimation of middle- and high-latitude ozone at 200 mbar is thus a GCM artifact, rather than a chemical shortcoming. During future model development, we will include the chemistry into a version of the GCM with higher vertical resolution in the tropopause region.

In the tropics and subtropics (Hilo at 20°N and Natal at 6°S in Figure 1, Pretoria at 26°S in Figure 2, and Samoa at 14°S which is not shown), the model does a reasonably good job of reproducing observed ozone amounts at 200 mbar, though there is a slight positive bias. The model has only slightly more variability than seen in the observations.

In the middle troposphere from about 800 to 300 mbar, the model reproduces both observed ozone abundances and the seasonal cycle fairly well. The model is able to capture the summer maximum seen at middle and high latitudes in the Northern Hemisphere. At 300 mbar, both the mean values and the standard deviations in the model agree well with the observations. At lower levels the model has more variability than is observed, even when its mean values agree quite well (e.g., Hohenpeissenberg at 500 mbar). In the tropics and subtropics the model reproduces fairly well the February-June maximum at Hilo, the September-November maximum at Natal, and the near lack of seasonality at Samoa (not shown). The variance of ozone values found in the model also agrees quite well with the measurements. In the Southern Hemisphere extratropics the model again captures the minimal seasonality at both Lauder and Syowa. The standard deviations agree fairly well at 300 mbar, but the model cannot reproduce the extremely small values reported for the observed standard deviations at 500 and 800 mbar.

Surface ozone values are simulated quite well in the model. The primary exception is at northern midlatitudes, where the modeled summertime values are too large. It is difficult to compare a 4 by 5 degree grid box with observations at a single point however. In the case shown in Figure 1, for Hohenpeissenberg, the model grid box which includes that relatively remote, unpolluted, hilltop site also includes many industrial cities in central Europe. At higher levels, where air has had more time to mix, this differential becomes less and less important, but at the surface it can be quite significant. Standard deviations of surface ozone mixing ratios appear to be overestimated in the model outside the tropics.

Figure 2 shows several ozone profile comparisons between observations and model values. Both the standard model run, and an alternate run with 60% less ozone in the stratosphere (which results in a 70% reduction in the flux of ozone from the stratosphere to the troposphere), are shown. In general, the standard simulation gives a fairly good reproduction of the observed profiles at most locations, with the simulated mean values lying within the standard deviation of the observations at all points except for Pretoria in January at upper levels, and



**Figure 1.** Comparison of observed and simulated annual cycles of ozone at the indicated altitudes and locations. Open triangles and dotted lines indicate ozonesonde measured mean values and standard deviations, respectively. Solid circles and dashed lines show modeled mean values and standard deviations. All values are mixing ratios in ppbv. The coordinates are, from left to right, Resolute (75°N, 95°W), Hohenpeissenberg (48°N, 11°E), Hilo (20°N, 155°W), Natal (6°S, 35°W), Lauder (45°S, 170°E), and Syowa (69°S, 39°E). Data records at these locations are from 5 to 15 years long and include between 217 and 1615 individual measurements [Logan, 1999].

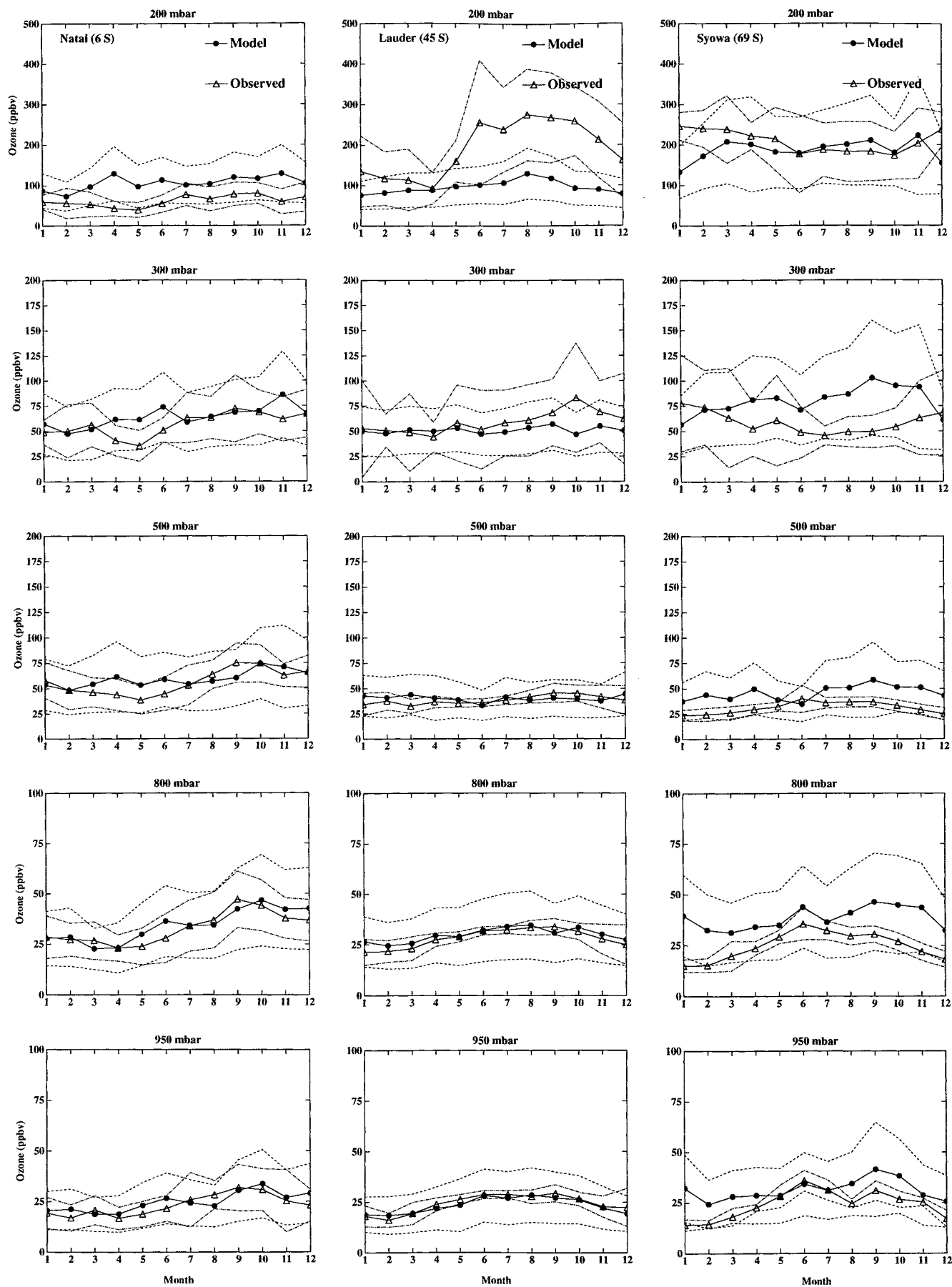
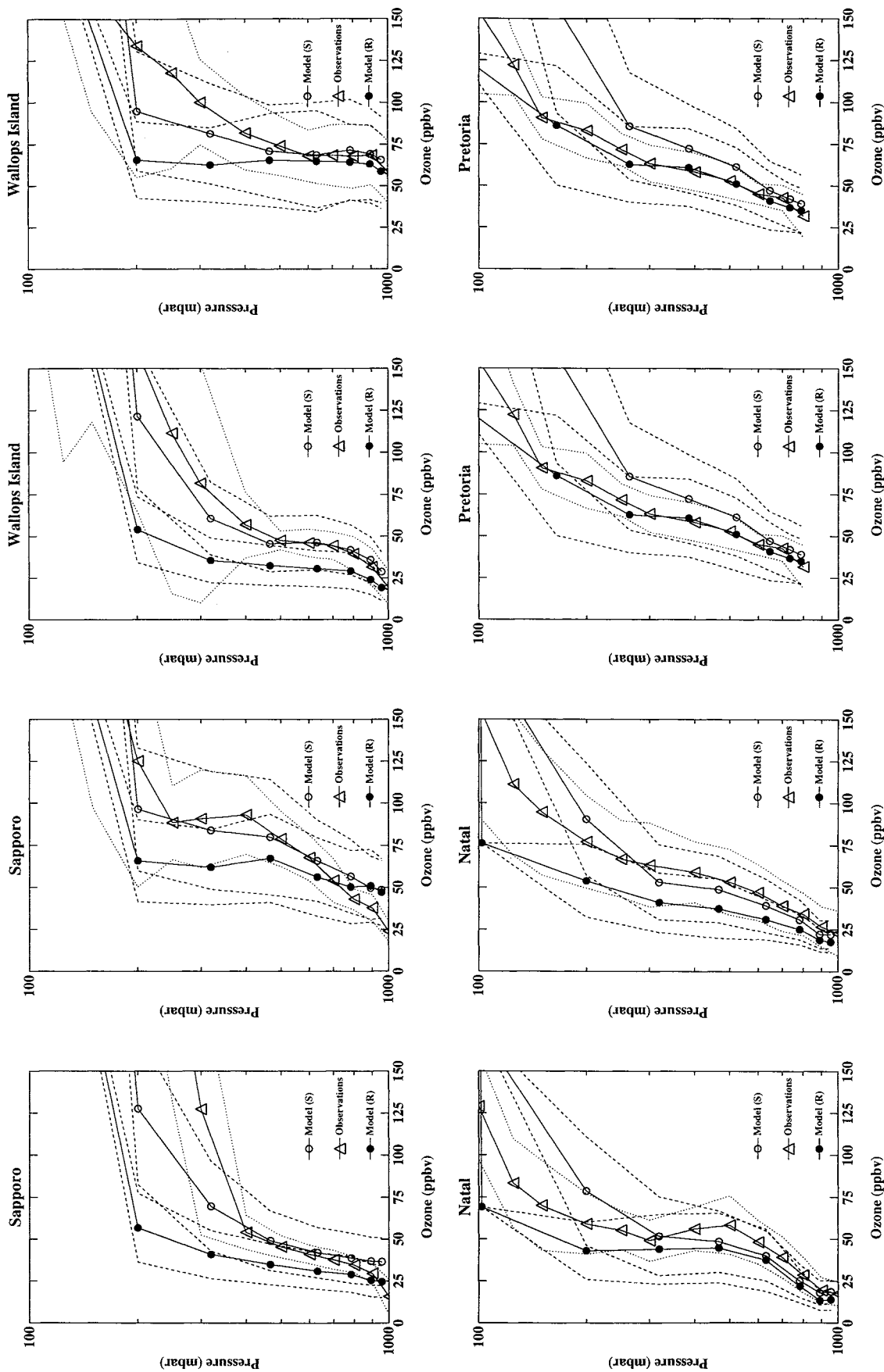
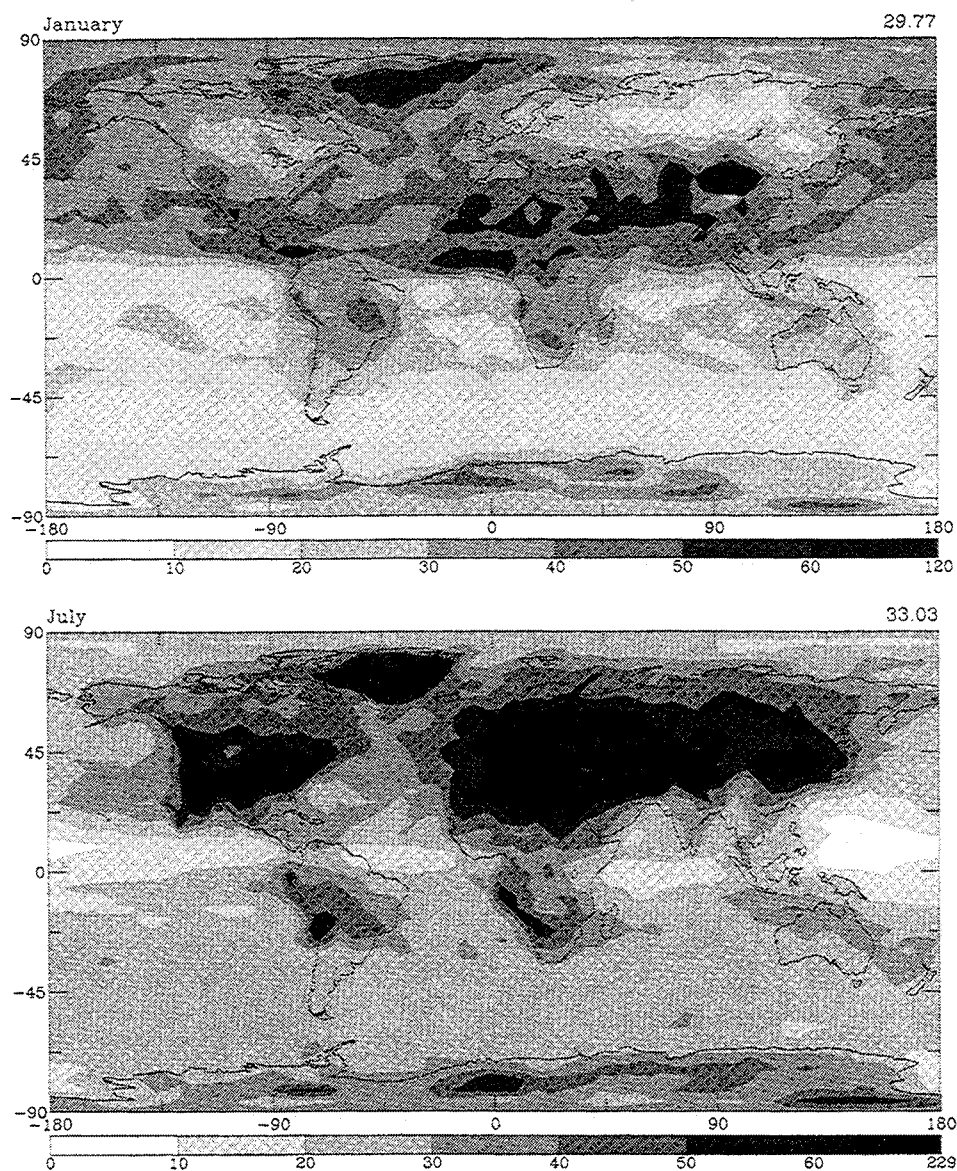


Figure 1. (continued)



**Figure 2.** Comparison of observed and simulated ozone profiles at the given locations in January (top row) and July (bottom row). Open triangles and dotted lines indicate ozonesonde measured mean values and standard deviations, respectively. Open circles and dashed lines show modeled mean values and standard deviations for the standard simulation (S), while filled circles and dashed lines are from the simulation with reduced ozone in the stratosphere (R). The coordinates of the locations are Sapporo (43°N, 141°E), Wallops Island (38°N, 76°W), Natal (6°S, 35°W), and Pretoria (26°S, 28°E). Data records at these locations are from 3 to 16 years long and include between 136 and 388 individual measurements [Logan, 1999].





**Figure 3.** Modeled ozone values (ppbv) in the lowest model layer for the present day. (top) January near-surface values, and (bottom) July values. Numbers in the upper right of each panel give area weighted global mean values for comparison with preindustrial values (Figure 12).

Sapporo, where the model values are too small at high levels in January, and too large at the surface year round. Based on the sonde/model comparisons, it is difficult to determine which simulation is better. A prime example of this difficulty is shown in the Pretoria comparisons, where the run with reduced stratospheric ozone clearly gives a better match to the observations than the standard run in January, but the opposite is true in July. While the upper levels of the Natal comparisons suggest that a stratosphere-to-troposphere ozone flux somewhere in between the two cases shown here would be best, the Wallops Island and Sapporo comparisons show that both simulations tend to underpredict upper level ozone. This is especially true at Sapporo during winter, when the stratosphere-troposphere flux is largest at northern midlatitudes. While omission of NMHCs from the model has likely reduced ozone production above 300 mbar by 0–20% [Wang *et al.*, 1998c], these results also indicate the importance of improving the representation of stratosphere-troposphere

exchange processes in the GCM. Furthermore, the ozone profiles at northern middle latitude are actually in excellent agreement with observations when compared relative to the tropopause height [Grewe *et al.*, 2001]. This suggests that much of the discrepancy shown in Figure 2 results from a poorly located model tropopause (typically too high at northern middle latitudes) rather than a chemical bias. This will likely improve as we move to a model with higher vertical resolution. However, recent observations indicate that at high  $\text{NO}_x$  levels, current understanding of ozone chemistry in the upper troposphere may also have deficiencies [Jaegle *et al.*, 1999]. This may be improved by recent revisions to two relevant reaction rates that are not yet incorporated into the model [Brown *et al.*, 1999; Portmann *et al.*, 1999].

Near surface ozone (values at the center of the lowest layer) is shown in Figure 3. January values are distinctly less than July values over the Northern Hemisphere polluted continental regions, due to enhanced photochemical ozone formation in

**Table 4.** Surface Ozone (ppbv)

	January West Africa Maximum	January, North Atlantic	July, Eastern United States	July, Southwest Africa Maximum	July, Coastal Antarctica, 30°-50°E
<i>Roelofs and Lelieveld</i> [1995]	30-40	20-25	30-50	40-50	10-15
<i>Müller and Brasseur</i> [1995]	30-35	35-45	40-50	28-35	12-18
<i>Collins et al.</i> [1997]	60-80	20-40	120-140	60-100	0-20
<i>Berntsen and Isaksen</i> [1997]	35-40	25-35	40-55	25-35	10-20
<i>Wang et al.</i> [1998b]	60-70	30-40	40-70	50-70	20-30
<i>Lawrence et al.</i> [1999]	20-30	20-30	30-40	30-50	10-20
<i>Mickley et al.</i> [1999]	70+	30-40	40-60	50-70	20-30
<i>Lelieveld and Dentener</i> [2000]	--	--	60-70	30-50	15-20
This work	60-65	30-50	50-80	30-60	20-30
Observations		Atlantic Islands, 30-40	Wallops Island (38°N, 76°W) 59 ± 18	Brazzaville (4°S, 14°E) 33 ± 6	Syowa (69°S, 39°E) 29 ± 5

<sup>a</sup>Values (in ppbv) are January and July monthly means, except in the following cases, where we used the closest available data: *Roelofs and Lelieveld* [1995] are December-February and June-August averages, *Müller and Brasseur* [1995] are for day 360 in December and day 180 in June, *Collins et al.* [1997] are for February and August, and *Lelieveld and Dentener* [2000] are for May-August. North Atlantic island observations are the January monthly mean range based on 4 years of data from Sable Island (44°N, 60°W) and 1 year of data from Azores (39°N, 28°W) as given by *Parrish et al.* [1998]. Ozone sonde data for Wallops Island, Brazzaville, and Syowa are from *Logan* [1999].

summer. Over the Southern Hemisphere continents, July values are also larger, primarily as a result of biomass burning. Values are larger over the continents in July, and in January for the Southern Hemisphere, but are larger over the oceans in January for the Northern Hemisphere (probably as a result of comparatively rapid continental deposition). These ozone distributions are fairly similar to those found in other models, though again there are large differences between model formulations. Sample comparisons are presented in Table 4. Most of the models agree fairly well over polluted areas such as the eastern United States. The models also generally agree with observations from Wallops Island. Though located at a relatively remote site off the American coast, this site receives polluted air in the outflow from the interior. All of the models simulate a July maximum over southwest Africa, though some

find values somewhat larger than those measured at Brazzaville. An interesting region is on the Antarctic coast near Syowa station, where many of the models are on the low side of the ozone sonde record. Since this region is far removed from most anthropogenic emissions, this may indicate problems with the basic chemistry or transport mechanisms used in these models. Similarly, several of the same models have lower values than observed over the relatively remote North Atlantic. The GISS model does a good job at all of these sites.

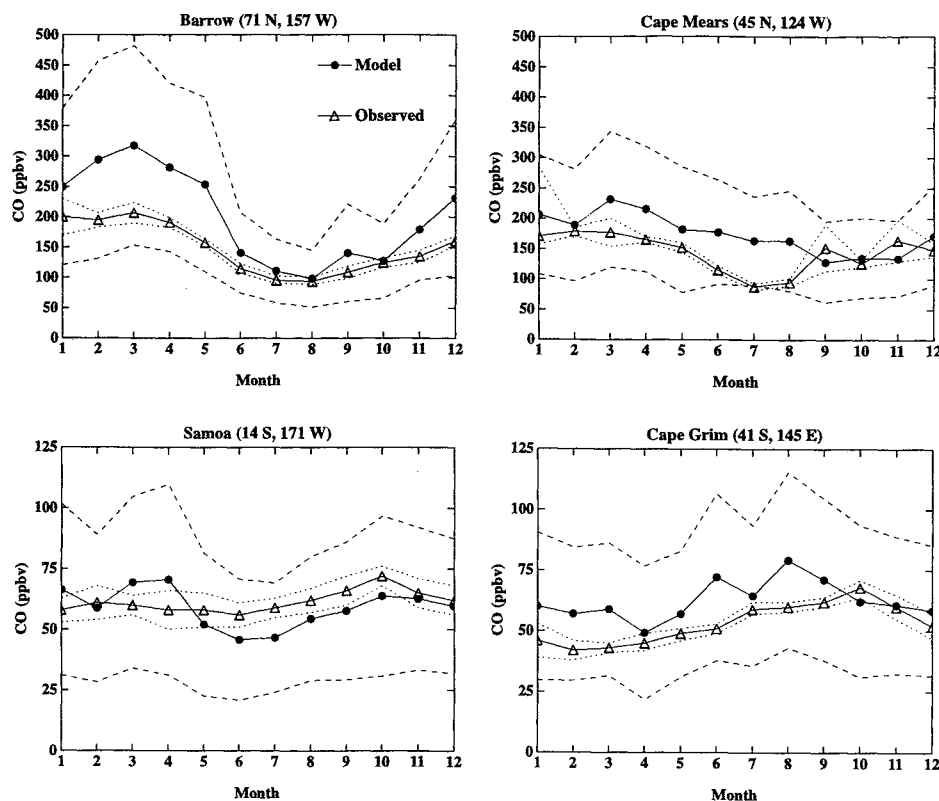
Large intermodel differences in the ozone budget (Table 5) are indicative of the large uncertainties remaining even after models are shown to reproduce the limited set of available observations. The net chemical ozone change, which is the difference between two large production and loss terms (~3500 Tg yr<sup>-1</sup> each), varies from -810 to +550 Tg yr<sup>-1</sup>. Our model lies

**Table 5.** Ozone Budget<sup>a</sup>

	Chemistry	Dry Deposition	Stratosphere	Burden
<i>Roelofs and Lelieveld</i> [1995]	+170	-740	+575	236
<i>Müller and Brasseur</i> [1995]	+550	-1100	+550	---
<i>Lawrence</i> [1996]	+30	-641	+594	---
<i>Berntsen and Isaksen</i> [1997]	+295	-1178	+846	---
<i>Levy et al.</i> [1997]	+128	-825	+696	298
<i>Roelofs et al.</i> [1997]	+75	-534	+459	271
<i>Houweling et al.</i> [1998]	-86	-681	+768	311
<i>Wang et al.</i> [1998b]	+420	-820	+400	310
<i>Hauglustaine et al.</i> [1998]	+507	-1237	+391	364
<i>Crutzen et al.</i> [1999]	-810	-620	+1440	---
<i>Lawrence et al.</i> [1999]	-478	-621	+1103	---
<i>Mickley et al.</i> [1999]	+370	-760	+390	360
<i>Stevenson et al.</i> [2000] <sup>b</sup>	+430	-862	+432	316
<i>Lelieveld and Dentener</i> [2000]	+140	-705	+565	347
This work	+389	-1140	+750	262

<sup>a</sup>Values are given in Tg yr<sup>-1</sup> for sources and sinks, and Tg for the total burden. All values are annual means. Note that *Mickley et al.* [1999], *Roelofs et al.* [1997], *Roelofs and Lelieveld* [1995], and this study used chemistry included within general circulation models, while the other studies used offline chemical transport models.

<sup>b</sup>D. S. Stevenson et al. (Future tropospheric ozone radiative forcing and methane turnover: The impact of climate change, submitted to *Geophysical Research Letters*, 2000).



**Figure 4.** Comparison of observed and simulated carbon monoxide near the surface. Open triangles and dotted lines indicate measured mean values and standard deviations, respectively. Solid circles and dashed lines show modeled mean values and standard deviations at the 959-mbar level.

within that range and is near the high end of the range for both ozone removal by dry deposition and influx from the stratosphere. Recent satellite observations suggest that the stratosphere-to-troposphere flux is between 450 and 590 Tg yr<sup>-1</sup> [Gettelman *et al.*, 1997], lower than the value seen in our model, as expected from tracer transport studies indicating that the nine-layer version of the GISS GCM has too much downward transport across the tropopause for the global, annual average [Rind *et al.*, 1999]. Since the abundance of ozone is a highly nonlinear function of the amount of ozone precursors, small changes in precursor species can also significantly affect the ozone budget. The total tropospheric ozone burden of 262 Tg is again within the range seen in other models with more detailed chemistry. To calculate this value, we have summed over all grid boxes with 150 ppbv or less ozone, using this threshold to define tropospheric air. If we simply sum over the lowest seven levels, we find an ozone burden of 422 Tg. As the model has very coarse resolution in the tropopause region, it cannot accurately discriminate stratospheric ozone, and therefore using the 150 ppbv threshold is more realistic. Since there is little chemistry and no deposition in the top layers, the source and sink terms over that region are insignificantly altered from those calculated for the bottom seven layers. Though this model does not include NMHC chemistry, this has been shown to have a fairly small effect on the total ozone budget [Wang *et al.*, 1998c], so has probably not greatly influenced these results. Furthermore, isoprene-generated carbon monoxide is included in the model, and isoprene accounts for about half of the overall effect of NMHCs (though some of these effects are via peroxy acetyl nitrate, which is also not included here) [Wang *et al.*, 1998c].

### 3.2. Carbon Monoxide

A comparison between the simulated annual cycle of carbon monoxide near the surface and observations [Novelli *et al.*, 1998] is shown in Figure 4. While the model overestimates the seasonal variation at the high northern latitude site, it does a fairly good job of matching the abundances at other latitudes, where it obtains agreement with observations similar to other models [e.g., Mickley *et al.*, 1999]. As in the case of ozone, the model produces the best results in the tropics and at southern middle latitudes. Variability in the model may be overestimated, however. The standard deviation of the model results is typically 5 to 10 times larger than observed, but the observations covered periods of only 4 to 7 years, and either the observations or the simulations could be subject to many of the same problems as discussed in the previous section for ozone.

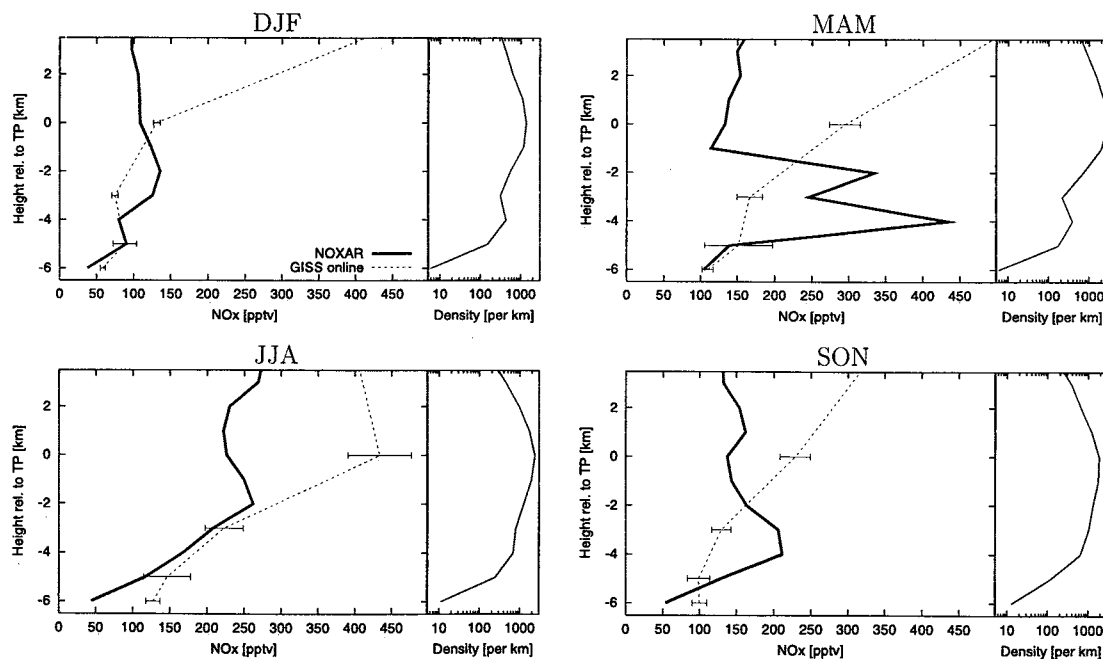
Few global data sets are available for tropospheric constituents. Carbon monoxide observations were taken by the Measurement of Air Pollution from Satellites (MAPS) experiment flown aboard the space shuttle [Connors *et al.*, 1999]. The instrument took measurements during October 1984, April 1994, and October 1994. Though short term, these measurements provide a useful comparison for a global model's distribution. Plate 1 shows carbon monoxide mixing ratios in the GCM and as observed by MAPS. The instrument samples the entire tropospheric column, with an averaging kernel centered at approximately 7–8 km altitude [Reichle *et al.*, 1999], and the mean value is shown here. Model output has been weighted according to the same profile. The April comparison shows that the model does a fairly good job

representing the overall meridional gradient in CO. The global average value is also accurately reproduced by the model. The largest values in the tropics and subtropics are in somewhat different locations, however. The model puts maxima over the continents, especially over Central America and East Africa. While the observations are relatively sparse, there seem to be larger values over the tropical Atlantic and over the western Pacific than seen in the model. The latter would presumably result from a large Asian source and may indicate that this source is underestimated in the GCM. The October comparison is more complex. The model shows very large CO values over South America, which also appear in the 1994 observations. However, the large values (greater than 120 ppbv) in the observations seem to extend over much of the Southern Hemisphere subtropics, while they are more confined to the continents in the GCM. The model is run with a compilation of emissions from 1985 through 1992, so that it seems sensible that it falls somewhere between the two observed periods. Interannual variability, though, makes it difficult to interpolate between the two individual years. For example, extremely large fires burned over Indonesia during 1994, making this an exceptional year for biomass burning emissions. Overall, the model appears to have a reasonable global distribution and magnitude in both seasons, though it generally underestimates CO due to the outflow of polluted continental air. In both April and October the model also has a low bias at Southern Hemisphere middle latitudes.

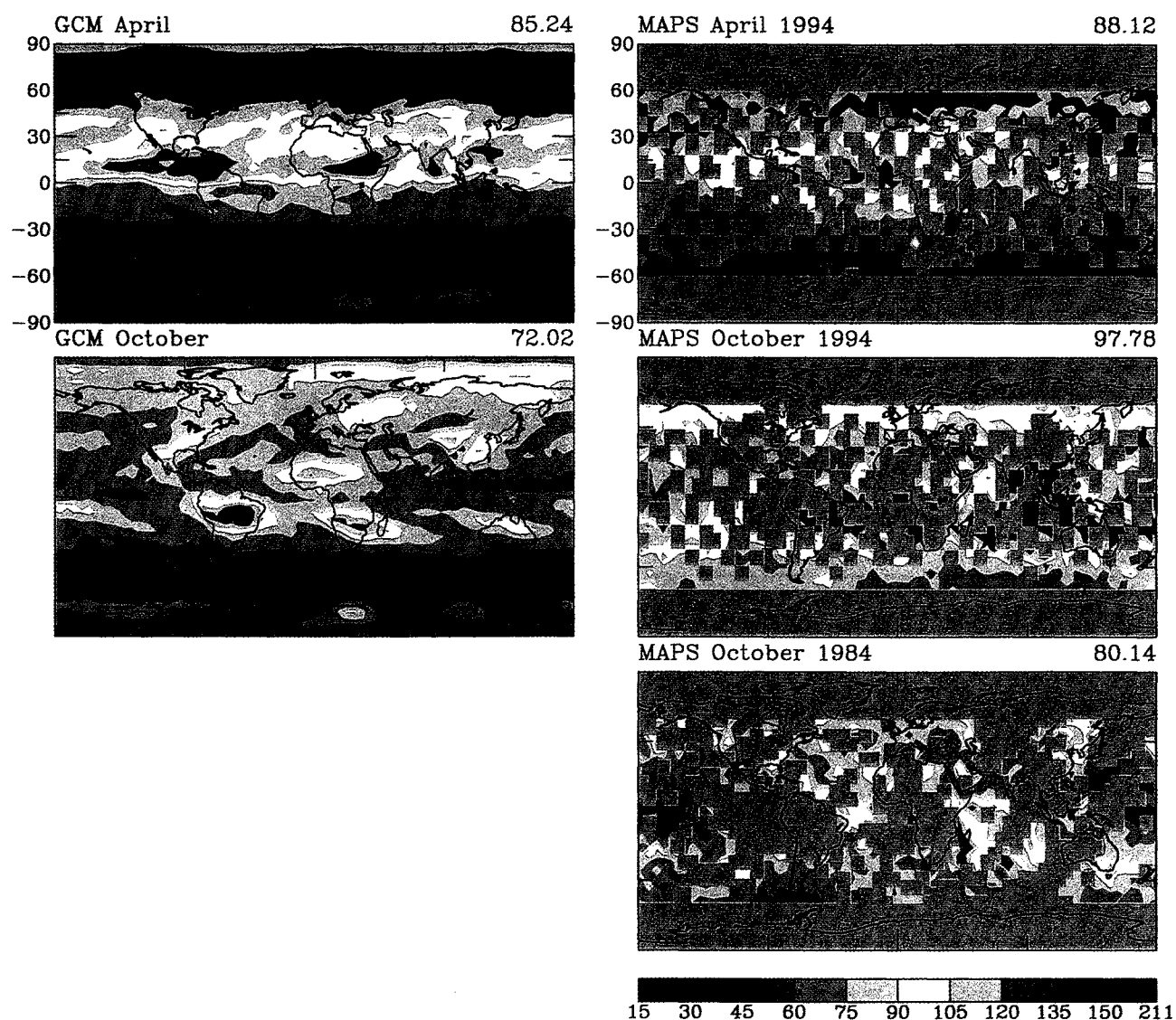
### 3.3. Nitrogen Oxides and Lightning

Comparison of modeled  $\text{NO}_x$  in the middle and upper troposphere with measurements obtained as part of the Nitrogen Oxides and Ozone Measurements Along Air Routes (NOXAR) program is shown in Figure 5 (see [Grewe *et al.*, 2001] for a more detailed comparison). The model generally reproduces the observed mixing ratios quite well in the middle

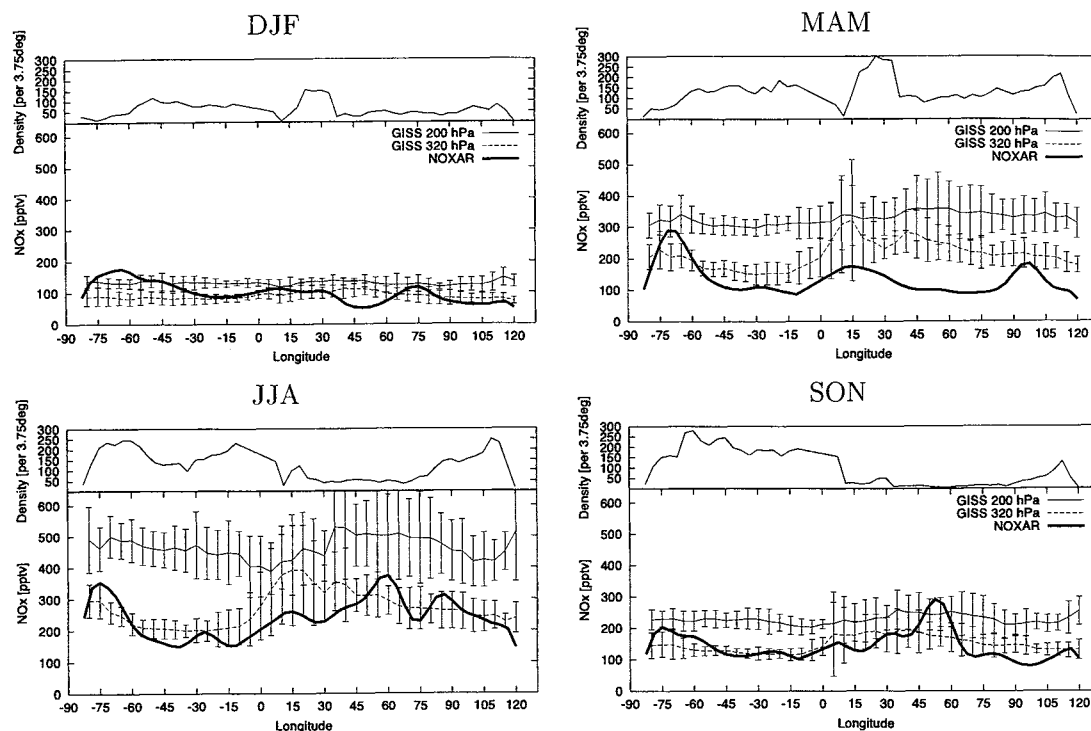
troposphere. It tends to underestimate nitrogen oxide abundances in the region from about 1 to 3 km below the tropopause, however, except during Northern Hemisphere summer. This may be a contributing factor to the underestimation of ozone at Northern Hemisphere mid-latitudes in this altitude range (Figures 1 and 2). At the altitude of the tropopause the model overestimates  $\text{NO}_x$ , except in northern wintertime. The mean values shown in Figure 5 can be misleading, as Grewe *et al.* [2001] showed that the most frequent  $\text{NO}_x$  values and the variability of  $\text{NO}_x$  at the tropopause are in good agreement with the observations, while the mean values are too high due to the rare occurrences of very large values. Additionally, the nine-layer version of the GISS model has fairly coarse vertical resolution near the tropopause (~3–4 km), making the determination of which level best represents near-tropopause conditions ambiguous. Therefore in Figure 6 we present  $\text{NO}_x$  values simulated at both the 200 and 320 mbar levels compared with the NOXAR observations at the tropopause. Simulations performed to isolate individual contributions to the  $\text{NO}_x$  budget showed that transport is the dominant influence at the 200 mbar level, while it is chemistry at the lower 320 mbar level [Grewe *et al.*, 2001]. Except for the northern spring, model values at 320 mbar do quite a good job of matching the measured values. The values at 200 mbar are quite a bit too large in spring and summer, though at least in spring, the vertical profile changes so sharply with altitude that the coarse model layers can be quite deceptive. These results imply that the chemistry scheme is in general doing a good job, while the dynamics near the tropopause need improvement (as seen in the ozone model/measurement comparison as well, though in those examples the stratospheric flux was too small, while here it seems too large, highlighting the complex temporal and geographical variability of stratosphere-troposphere exchange). The longitudinal variations seen by the aircraft instrument, with maxima over continental regions, are captured to a limited



**Figure 5.** Seasonal mean values of  $\text{NO}_x$  ( $\text{NO} + \text{NO}_2 + \text{NO}_3$ ) volume mixing ratios (ppbv) in the middle and upper troposphere. Profiles measured by the NOXAR aircraft, which flew almost entirely between  $40^\circ$  and  $60^\circ\text{N}$ , and  $90^\circ\text{W}$  to  $120^\circ\text{E}$  (heavy line) [Grewe *et al.*, 2001] and simulated by the GCM for the same locations (dotted line with 1 standard deviation uncertainties) are shown. The density of aircraft measurements is shown on the right side of each plot.



**Plate 1.** Observed and modeled global carbon monoxide (column mean mixing ratio in ppbv). Measurements were taken by the Measurement of Air Pollution from Satellites (MAPS) instrument. (top) Values for April (observations from 1994, model values from the “present day” simulation), and (middle) similar plots for October. (bottom right) Measurements taken 10 years earlier, during October 1984. Model output has been weighted similarly to MAPS (see text for details), so that the two values are comparable. All plots use the same color scale.



**Figure 6.** Measured  $\text{NO}_x$  in the tropopause region ( $\pm 25$  mbar relative to the local tropopause) from NOXAR as in Figure 5. The nearest GISS model levels at 200 hPa and 320 hPa are shown as thin and dashed lines, respectively. The interannual standard deviation is also included for the models (bars). The number of NOXAR measurements per 3.75 degrees is shown along the top of each plot.

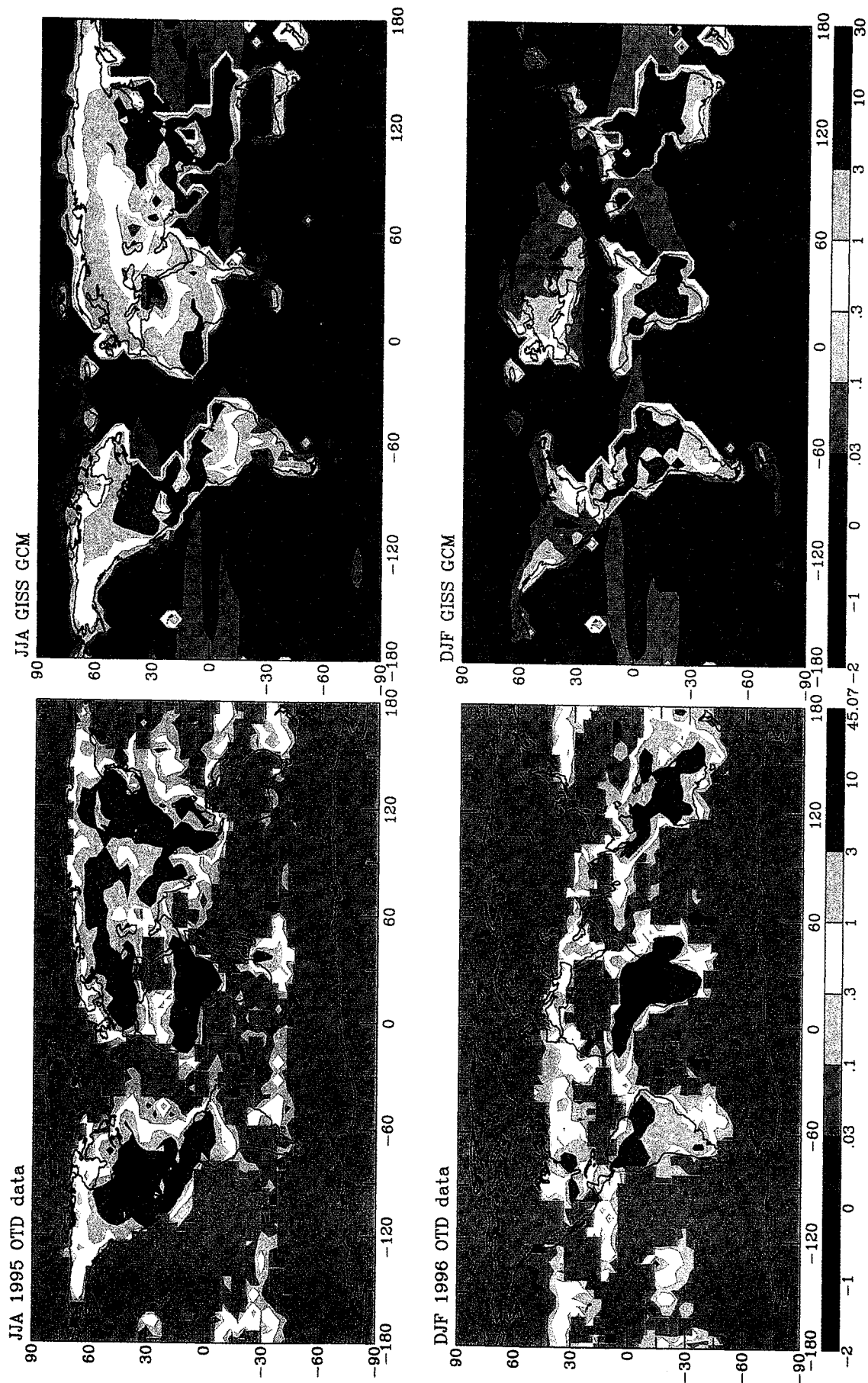
extent by the model. The model tends to give a more uniform distribution (especially at 200 mbar), as does the European Center Hamburg (ECHAM) model, version 3 [Schumann *et al.*, 2000] and version 4 [Grewe *et al.*, 2001]. Significant land-ocean contrasts are seen in most seasons at 320 mbar in the GISS GCM, where chemistry largely governs the  $\text{NO}_x$  abundance. While the lack of NMHCs in the model could affect the results, it is not likely that it is responsible for the land-ocean contrast being somewhat reduced in the model as compared with observations. NMHCs lead to decreased  $\text{NO}_x$  concentrations in the upper troposphere over continental regions where convection occurs [Wang *et al.*, 1998c], so would act to further reduce this contrast. The overall nitrogen oxide budget is shown in Table 3.

Overall, the model reproduces the large variation between summer and winter reasonably well but misses the upper tropospheric maxima seen in observations during both equinox seasons. These maxima were also missed in the ECHAM4 model [Grewe *et al.*, 2001]. While there is some evidence that the nine-layer version of the GISS GCM has too little downward transport from  $40^\circ$ – $60^\circ\text{N}$  during both April and October [Rind *et al.*, 1999], which could account for some of this discrepancy, it also seems to have too much downward transport during December, which is not seen in the present model/measurement comparison. More likely the two models both fail to calculate enough in situ production, due to too little transport of ozone precursors up from the boundary layer and/or too little production of  $\text{NO}_x$  from lightning at Northern Hemisphere middle latitudes.

A comparison of lightning flash frequencies observed by the Optical Transient Detector satellite instrument [Boccippio *et al.*, 1998] and simulated in the GISS GCM is shown in Plate 2. The model parameterization generates lightning interactively with the GCM's convection scheme [Price and

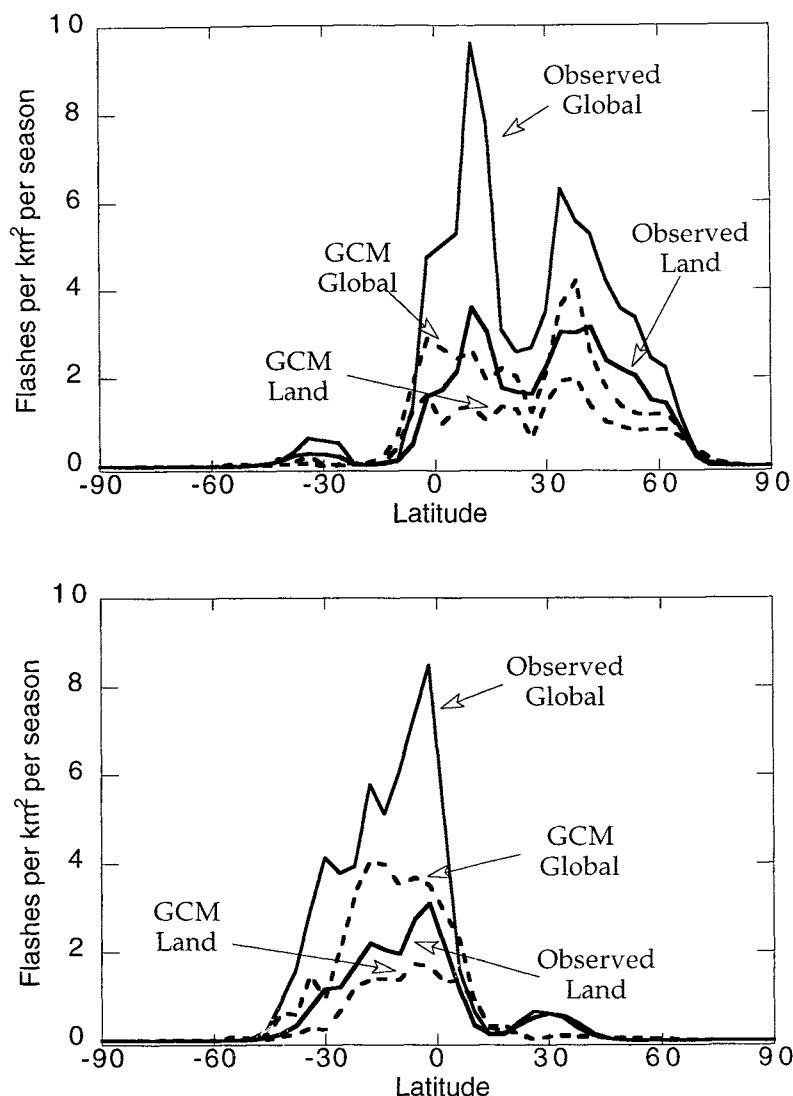
Rind, 1994; Price *et al.*, 1997]. The final lightning flash frequency in the model thus depends on both parameterizations, making it difficult to determine which is responsible for areas of disagreement (or even to be completely sure that correct areas do not result from a fortuitous cancellation of errors). These topics clearly deserve further study beyond the scope of this paper.

The model's flash frequency field captures some of the main features of the observed spatial distribution of lightning, including the large frequencies seen over tropical and subtropical continental regions. The global average flash rates in the model are only 60–65% of the observed values, however. Some local deficiencies are also apparent. In the tropics the model has a local maximum over the Indonesian archipelago during both seasons, while the observations favor Africa (though this could be a sampling bias). Similar results are seen in the observations for other years. The model parameterization also fails to reproduce observed lightning flash rates off the eastern edge of the continents (and over the oceans in general), especially over the western Atlantic, and off of southern Africa and Australia. The model underestimates continental lightning flash rates at northern midlatitudes over the continents as well, despite allowing overshooting of the top of a convective plume by one model layer in regions of very strong convection, such as at northern middle latitudes. The model's underestimation can be clearly seen in the comparison of zonal mean lightning flash rates shown in Figure 7, which reveals large model deficiencies over the oceans, as well as a distinct model underestimations over land which is largest from about  $40^\circ\text{N}$  to  $60^\circ\text{N}$  during June–August. A closer examination of the local flash frequencies shows that the model gives a flash rate up to an order of magnitude lower than observed over much of midlatitude Eurasia. This underestimation suggests that underprediction of model ozone



**Plate 2.** Lightning flash frequency (flashes  $\text{km}^{-2}$  per season). (top) June-August data, and (bottom) December-February data. (left) Values observed from June 1995 to February 1996 (other years are fairly similar) by the Optical Transient Detector instrument [Boccippio *et al.*, 1998], and (right) 9-year average from the model simulation.





**Figure 7.** Zonal mean lightning flash frequency (flashes  $\text{km}^{-2}$  per season) during (top) June-August and (bottom) December-February calculated from the data and simulations shown in Plate 2.

in some regions may be at least partially due to too little in situ production. This finding is in agreement with other model studies [e.g., Grewe *et al.*, 2001] and with observational evidence [e.g., Graustein and Turekian, 1996; Jeker *et al.*, 2000].

The production of nitrogen oxides from lightning involves further assumptions about the energy density per flash and the production amount per unit energy that are more difficult to validate. The total production is shown in Figure 8. Despite the underestimation of flash rates, our value of  $3.9 \text{ Tg yr}^{-1}$  is close to the “best” estimate of  $5 \text{ Tg yr}^{-1}$  and well within the expected range of 2 to  $20 \text{ Tg yr}^{-1}$  [World Meteorological Organization, 1999].

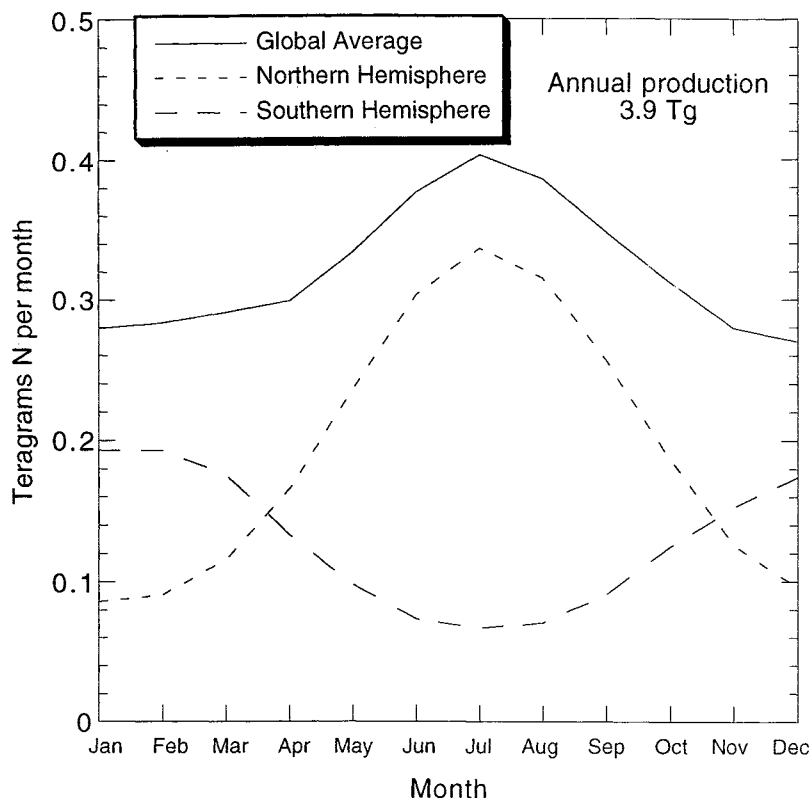
### 3.4. Hydrogen Peroxide

A comparison of the model’s hydrogen peroxide vertical profiles with aircraft observations (as given by Wang *et al.* [1998b], Mickley *et al.* [1999], and Koch *et al.* [1999]) is shown in Figure 9 (the model’s hydroxyl distribution is shown in Figure 13, discussed in section 4). The model does a fairly good job of reproducing the observed profiles in the northern

subtropics based on the Japan coast ( $\sim 35^\circ\text{N}$ ,  $145^\circ\text{E}$ ) and East China Sea regions ( $\sim 25^\circ\text{N}$ ,  $130^\circ\text{E}$ ). It is also able to capture the large abundances seen in the tropical South Atlantic ( $\sim 10^\circ\text{S}$ ,  $20^\circ\text{W}$ ) and southern Africa ( $\sim 15^\circ\text{S}$ ,  $25^\circ\text{E}$ ) regions during the September biomass burning season. However, the large values seen during September over the southern Brazilian coast ( $\sim 30^\circ\text{S}$ ,  $50^\circ\text{W}$ ) are not captured in the model, suggesting that emissions from biomass burning in South America may be too low (though the limited available data may not be representative of the longer term average). In the tropics the model greatly overestimates low-level (below about 600 mbar) amounts in the western equatorial Pacific ( $\sim 5^\circ\text{N}$ ,  $150^\circ\text{E}$ ) and western Pacific ( $\sim 10^\circ\text{N}$ ,  $155^\circ\text{E}$ ) regions. At the same time, however, the model reproduces observations from the Pacific Exploratory Mission (PEM) - Tropics, in both the polluted eastern Pacific and the remote central Pacific locals.

The GCM has roughly 50% more water vapor near the surface in the equatorial region than at  $25^\circ\text{N}$  (East China Sea region), suggesting that the large hydrogen peroxide values at low altitudes near the equator may be due to chemical production. A comparison between the hydrogen peroxide budget derived here and that of Koch *et al.* [1999], given in





**Figure 8.** Seasonal cycle of nitrogen oxide production from lightning in the present-day simulation. The result is a 9-year average.

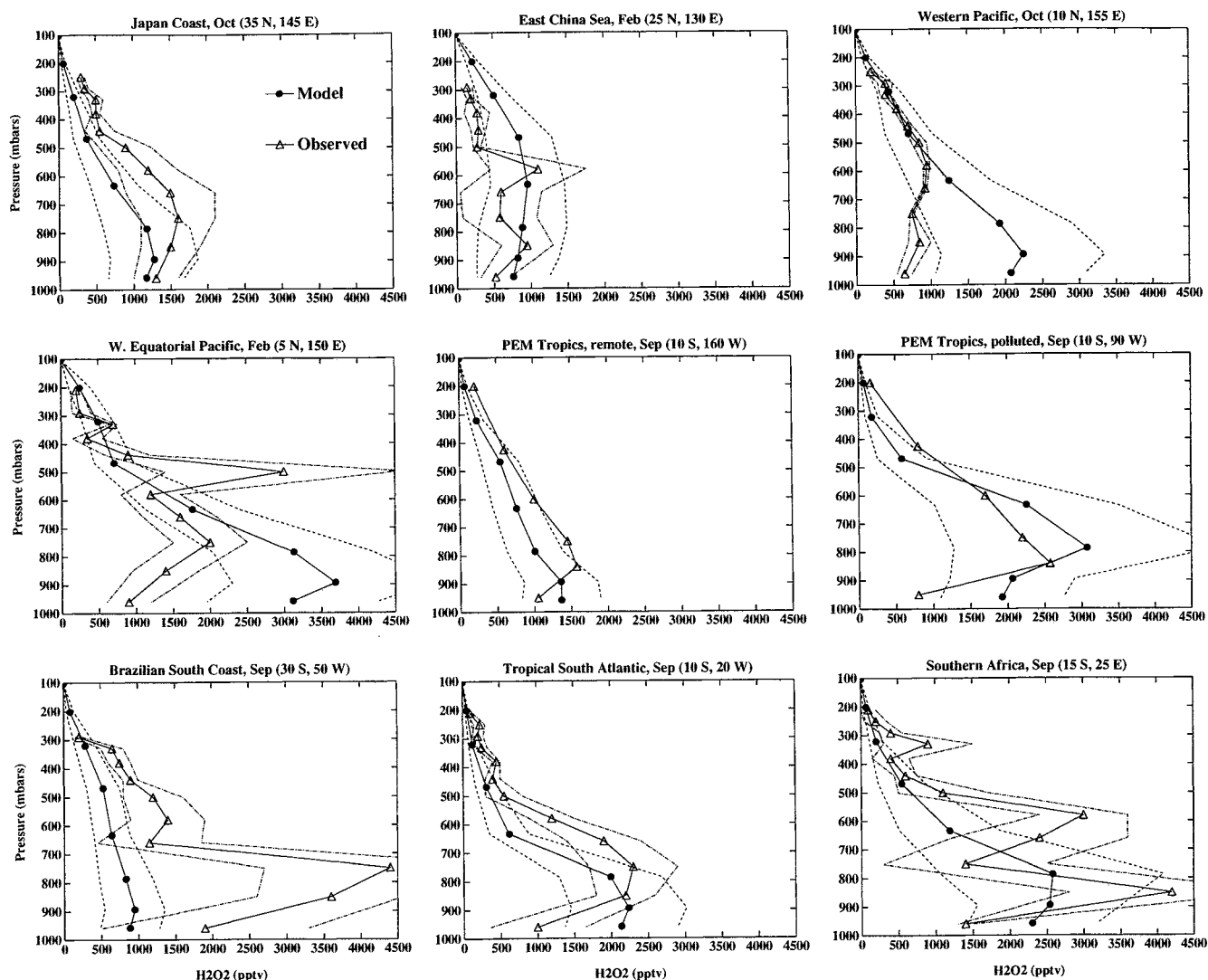
Table 6, shows that while chemical production is indeed 20% larger, at the same time, the wet removal of  $\text{H}_2\text{O}_2$  is 70% greater in this model, dry deposition at the surface is 38% less, and the tropospheric burden is also larger overall. Thus several factors lead to the large abundances at low levels in this model. The differences are especially large near the equator, where this chemistry model predicts much more hydrogen peroxide than was found in the *Koch et al.* [1999] simulations that used a prescribed OH distribution. At middle and high latitudes, differences between the two models are quite small. The results from this model are also fairly similar to those shown by *Wang et al.* [1998b] and *Mickley et al.* [1999], which also failed to simulate the very large abundances associated with South American biomass burning, though those models did not overestimate low-altitude  $\text{H}_2\text{O}_2$  over the western Pacific to as large an extent. Given the limited spatial and temporal coverage of the aircraft campaigns, it is difficult to clearly assess biases in the GCM. It seems, however, based on the western Pacific comparisons, that this model likely has too much low-level  $\text{H}_2\text{O}_2$  in the equatorial region, especially in the western Pacific. This may be related to outflow of polluted continental air from Asia.

#### 4. Response to Preindustrial Conditions

In order to use this model for studies of the interaction between chemistry and climate, we must examine not only how well the model can simulate current conditions, but how it responds to changes. While little observational data are available from the preindustrial period, many other models have looked at the changes from the preindustrial to the present, making this a useful benchmark of model sensitivity.

We therefore evaluate our model with respect to other models containing more detailed chemistry schemes by comparison of simulations using preindustrial conditions. For the preindustrial simulations, concentrations of long-lived greenhouse gases were reduced as follows:  $\text{CO}_2$  from 365 to 280 ppmv,  $\text{N}_2\text{O}$  from 314 to 275 ppbv,  $\text{CH}_4$  from 1.745 to 0.700 ppmv, and CFCs were reduced to zero. Emissions of ozone precursors were set to assumed preindustrial values, so that  $\text{NO}_x$  and CO emissions from fossil fuel burning and aircraft were set to zero, while those from biomass burning were set to one tenth their present-day values, as given by *Mickley et al.* [1999].  $\text{NO}_x$  emissions from soils were unchanged. Sulfate was set to natural background levels, assuming no anthropogenic component, as calculated in the GISS model [*Koch et al.*, 1999]. Sea surface temperatures and sea ice coverage derived from a mixed layer ocean run for preindustrial conditions performed with an earlier version of this model (8 by 10 degree resolution) were used as the boundary conditions for the tropospheric chemistry simulation. Surface temperature changes between the present-day simulations and the preindustrial are shown in Figure 10. Values over the oceans reflect the warmer sea surface temperatures and decreased sea ice coverage of today's climate. Model results for preindustrial conditions are taken from the last 8 years of 10-year runs, as 2 years were required for the model to equilibrate from present-day conditions.

Tropospheric ozone has increased significantly since the beginning of the industrial age. Figure 11 shows zonal mean present-day ozone mixing ratios, and the change from preindustrial to the present in units of mixing ratio and in percent, relative to the preindustrial amounts. Seasonal zonal mean ozone changes are shown in part 2. Table 7 presents the pre-industrial ozone budget (the tropospheric burden has been



**Figure 9.** Comparison of observed and simulated hydrogen peroxide profiles at the indicated locations. Open triangles and dotted lines indicate aircraft measured mean values and standard deviations, respectively. Solid circles and dashed lines show modeled mean values and standard deviations. The coordinates at the approximate center of the regions are shown. See Wang *et al.* [1998b] and Koch *et al.* [1999] for exact areas of aircraft campaigns.

calculated using a 150 ppbv threshold to exclude stratospheric air, as for the present day). From Figure 11, it is clear that most of the increase has been in the Northern Hemisphere, where ozone abundances have increased by 20–40 ppbv in most of the troposphere northwards of 20°N, in good agreement with the simulation of Stevenson *et al.* [1998]. This represents more than a doubling of ozone in most of the lower troposphere, as seen by Mickley *et al.* [1999]. At northern midlatitudes near the surface, values have increased by more than 125%. Ozone

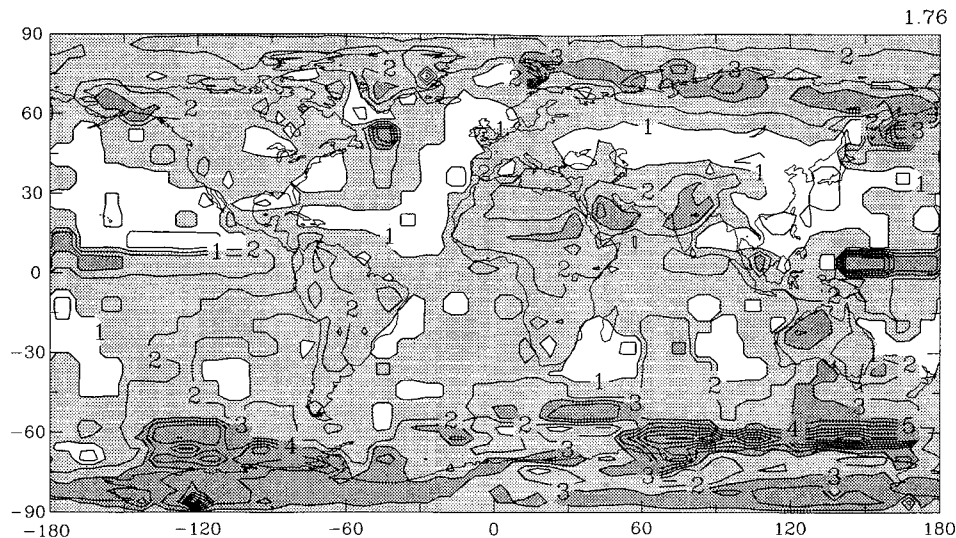
in the uppermost troposphere has increased by only 10–25%. As ozone at these altitudes is most important for climate change, the impact of ozone on climate has been much less than if the ground level increases persisted throughout the troposphere. We find an overall increase in the tropospheric ozone burden of 45%, in accord with the 25–57% range seen in other model studies (Table 7). This results primarily from decreased chemical production of ozone in the relatively unpolluted preindustrial atmosphere. In fact, the net contribution to the ozone budget from photochemistry is negative during the preindustrial period (–158 Tg yr<sup>–1</sup> in our model, –30 to –323 Tg yr<sup>–1</sup> in all studies), while it is positive in the present day in nearly all models.

Surface ozone is also much reduced in the preindustrial period, shown in Figure 12, as compared with the present day (Figure 3). The global mean surface mixing ratio has increased by 57% from the preindustrial to the present in January, and by 72% in July. For the annual average, the increase was 76% globally, with a 120% increase in the Northern Hemisphere, and a 31% increase in the Southern Hemisphere. Levy *et al.* [1997], using a chemical transport model, gave fairly similar

**Table 6.** H<sub>2</sub>O<sub>2</sub> Budget<sup>a</sup>

	This work	Koch <i>et al.</i> [1999]
Dry chemistry	+360	+300
Dry deposition	–88	–141
Wet deposition	–236	–125
Wet chemistry	–34	–34
Loss to stratosphere	–2	--
Burden	6.4	4.2

<sup>a</sup>Values are given in Tg yr<sup>–1</sup> for sources and sinks and Tg for the total burden. All values are annual means.

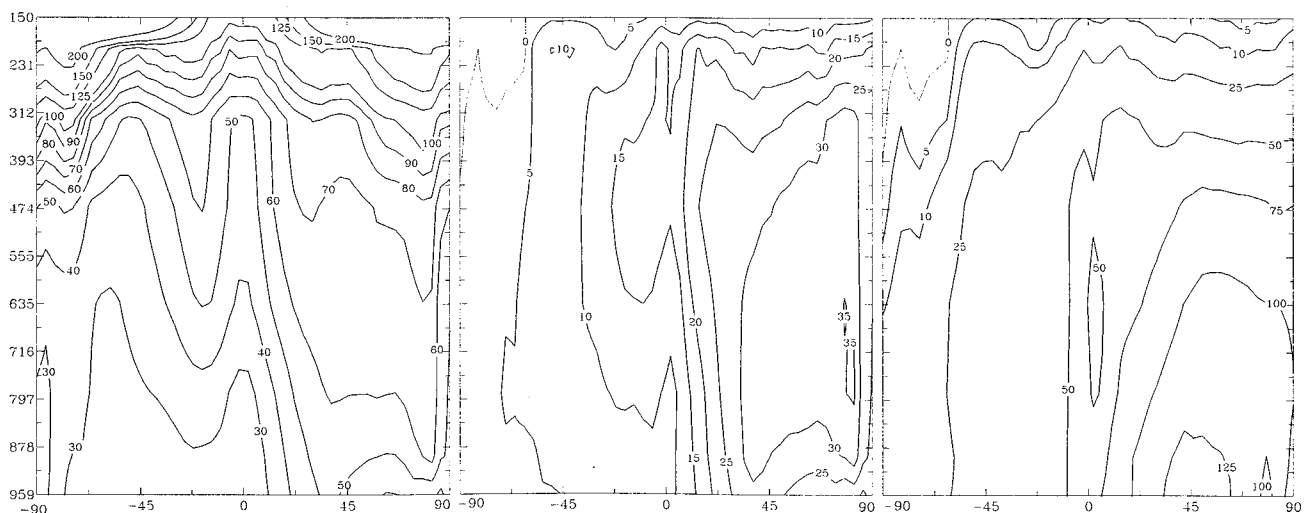


**Figure 10.** Annual average surface temperature change from the preindustrial to the present calculated in the model. Ocean changes primarily reflect the sea surface temperature and sea ice coverage changes which are prescribed based on an earlier run of the GISS GCM. The global mean temperature increase is 1.76 K. The contour interval is 1 K. Values below 1 are white, those between 1 and 3 are shaded light grey, and those above 3 are darker grey.

numbers, though a somewhat smaller interhemispheric difference. They found a global increase of 66% in boundary layer ozone from preindustrial to present, divided up into 73% in the Northern Hemisphere extratropics, 71% in the tropics, and 43% in the Southern Hemisphere extratropics. Very large differences from pre-industrial to present in our model are seen over the continents year round, but also over the Northern Hemisphere oceans all the way to the equator during January. Another region of note is the northern portions of the Northern Hemisphere continents during July, which had ozone levels similar to the remote ocean during the preindustrial period, but are fairly polluted during the present.

Our values are qualitatively similar to those shown by *Mickley et al.* [1999]. Both have patches of ozone below 10 ppbv over the tropical oceans, and fairly large areas with between 20 and 30 ppbv ozone over the Southern Ocean during

July, but not during January. Our model tends to have somewhat larger values over the Northern Hemisphere continents during July (20–40 ppbv versus 15–30 ppbv), but not during January. The GISS values are also similar to those presented by *Lelieveld and Dentener* [2000], who also found ozone levels below 10 ppbv over the tropical oceans, and between 20 and 30 ppbv over the Southern Ocean. Their May–August surface ozone (they do not show January), with values from 20 to 40 ppbv, are closer to those given by the GISS model than those given by *Mickley et al.* [1999]. The Lelieveld and Dentener model found much lower preindustrial surface ozone levels over Antarctica than the other two, however (as for the present day, see Table 4). *Roelofs et al.* [1997] show modeled pre-industrial surface ozone levels at Payerne (47°N) and Mace Head (53°N), which are both in the range of 10–20 ppbv during July, closer to the smaller *Mickley et al.* [1999] values than the amounts



**Figure 11.** Zonal mean ozone and ozone changes in the model. (left) Zonal mean present-day ozone mixing ratios. (middle) The change from preindustrial to the present in units of mixing ratio (ppbv). (right) The same change from preindustrial to the present, but in percent relative to the preindustrial amounts.

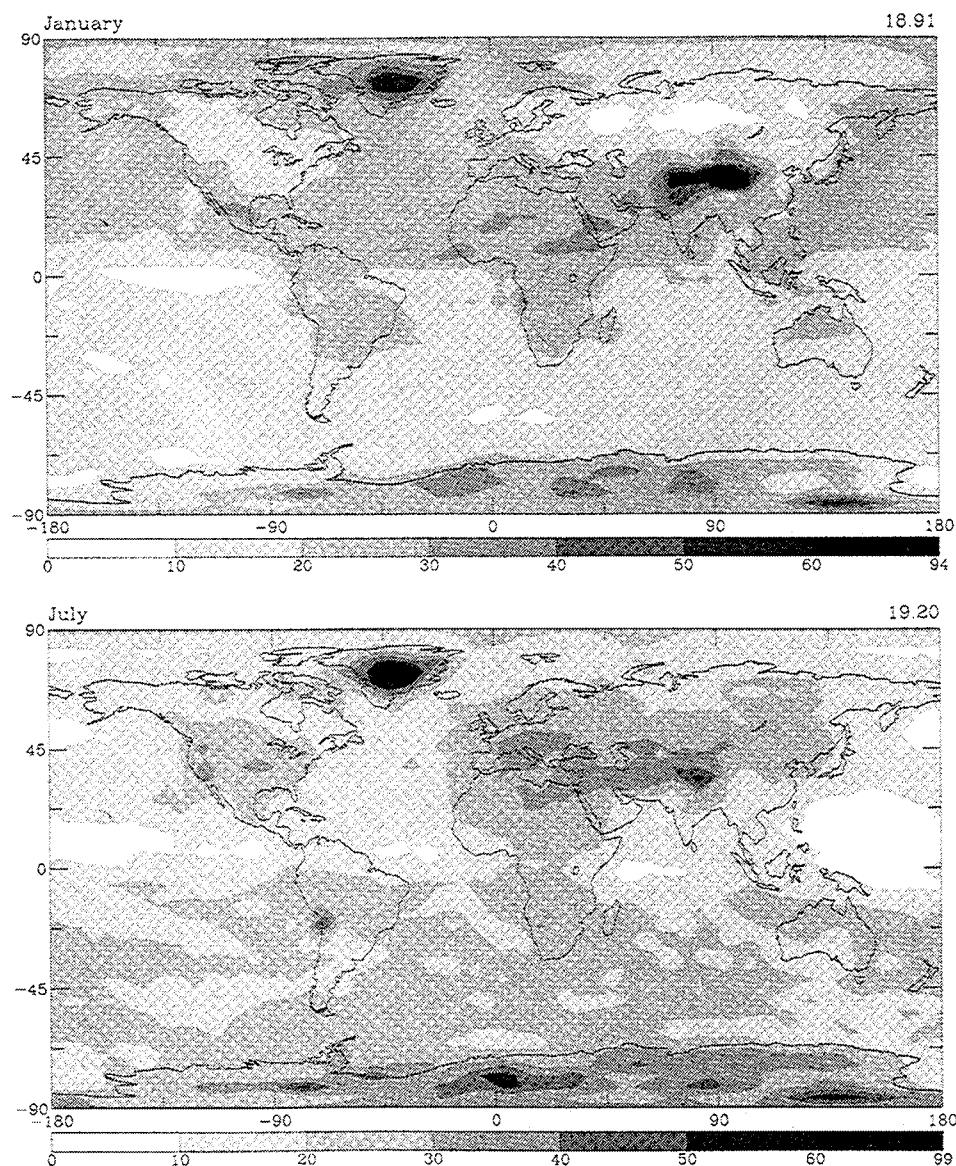
**Table 7.** Preindustrial Ozone Budget<sup>a</sup>

	Chemistry, Tg yr <sup>-1</sup>	Dry Deposition, Tg yr <sup>-1</sup>	Stratosphere, Tg yr <sup>-1</sup>	Burden, Tg	Burden Increase to Present, Tg
<i>Levy et al.</i> [1997]	-234	-459	+696	215	83 (39)
<i>Roelofs et al.</i> [1997]	-323	-296	+622	190	81 (43)
<i>Mickley et al.</i> [1999]	-30	-360	+390	230	130 (57)
<i>Lelieveld and Dentener</i> [2000]	-162	-444	+606	278	69 (25)
This work	-158	-625	+782	180	82 (45)

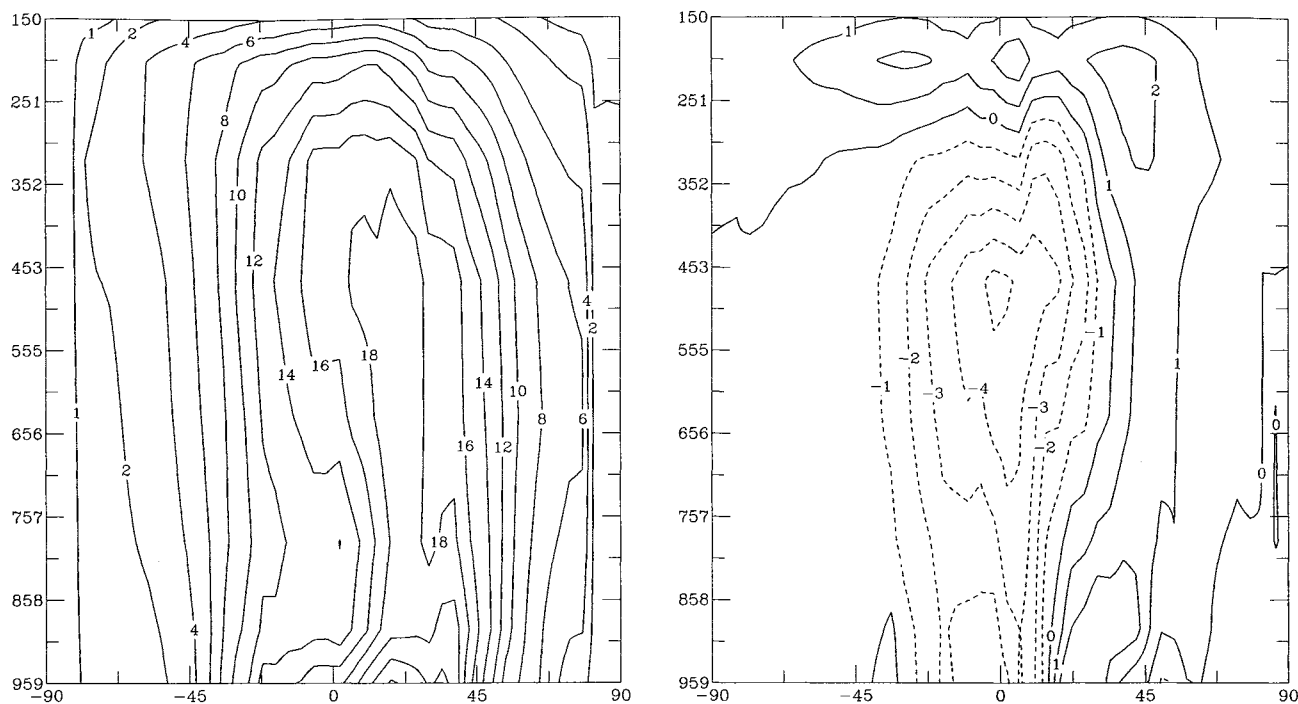
<sup>a</sup>Values in parentheses in the last column show percentage increases in the tropospheric ozone burden from preindustrial to the present, relative to the pre-industrial burden. All values are annual means.

given by *Lelieveld and Dentener* [2000] or in this work. The variations are perhaps indicative of the uncertainty surrounding preindustrial surface ozone levels. As discussed by *Wang and Jacob* [1998], most models find surface ozone values that are larger over Europe and South America than what little data are available [*Marenco et al.*, 1994].

The oxidation capacity of the troposphere may have also changed since preindustrial times. This could greatly impact the chemical lifetimes of many trace gases which are radiatively or chemically important, such as chlorofluorocarbons, carbon monoxide, methane, and other hydrocarbons. Our simulation shows a net decrease in the



**Figure 12.** Near surface modeled ozone values (ppbv) in the preindustrial period. (top) January values in the lowest model layer, and (bottom) July values. Large values over Greenland, the Himalayas, and Antarctica result from the model's use of terrain following coordinates, so that the lowest model level is at a much higher altitude in these regions where the orography is high. Numbers in the upper right of each panel give area weighted global mean values for comparison with present-day values (Figure 3).



**Figure 13.** (left) Zonal mean hydroxyl in the present-day simulation, and (right) the zonal mean hydroxyl change from the pre-industrial to the present. Both panels give values in units of  $10^5$  molecules  $\text{cm}^{-3}$ .

tropospheric oxidation capacity from the preindustrial to the present through most of the tropics and in the Southern Hemisphere, with an increase in most of the Northern Hemisphere extratropics (Figure 13 - Seasonal changes are shown in part 2). The modeled global mean OH abundance for the present day was  $9.76 \times 10^5$  molecules  $\text{cm}^{-3}$ , while the preindustrial value was  $10.37 \times 10^5$  molecules  $\text{cm}^{-3}$ . Globally, this represents a net decrease of 5.9% since the preindustrial period. Note that the present-day value agrees quite well with the  $9.7 \pm 0.6 \times 10^5$  molecules  $\text{cm}^{-3}$  derived from observations of the lifetime of the solvent methyl chloroform [Prinn *et al.*, 1995]. A range of results has been found in other models. Brasseur *et al.* [1998] found a decrease of 17% in global OH, Mickley *et al.* [1999] found a decrease of 16%, Wang and Jacob [1998] found a 9% decrease, and Bernsten *et al.* [1997] found a 6% increase. Several lower-dimensional models also found decreases in global OH from the preindustrial to the present [Thompson, 1992]. Assumed conditions during the preindustrial era vary widely from model to model, as emissions such as those from biomass burning are not well known, which may account for some of the large spread in the model results. We also note that our runs included altering not only emissions of ozone precursors to preindustrial levels, but also lowering sulfate aerosol, greenhouse gases, and ocean temperatures and sea ice coverage. These modifications are not commonly included, but all affect OH abundances. Increased temperatures and humidity in the present day both enhance OH, while the greater amount of sulfate reduces  $\text{NO}_x$  and hence OH. The net effect is to reduce the preindustrial to present-day decrease in the oxidation capacity of the troposphere by about half, as discussed more fully in part 2, likely accounting for our falling at the low end of the range seen in other models.

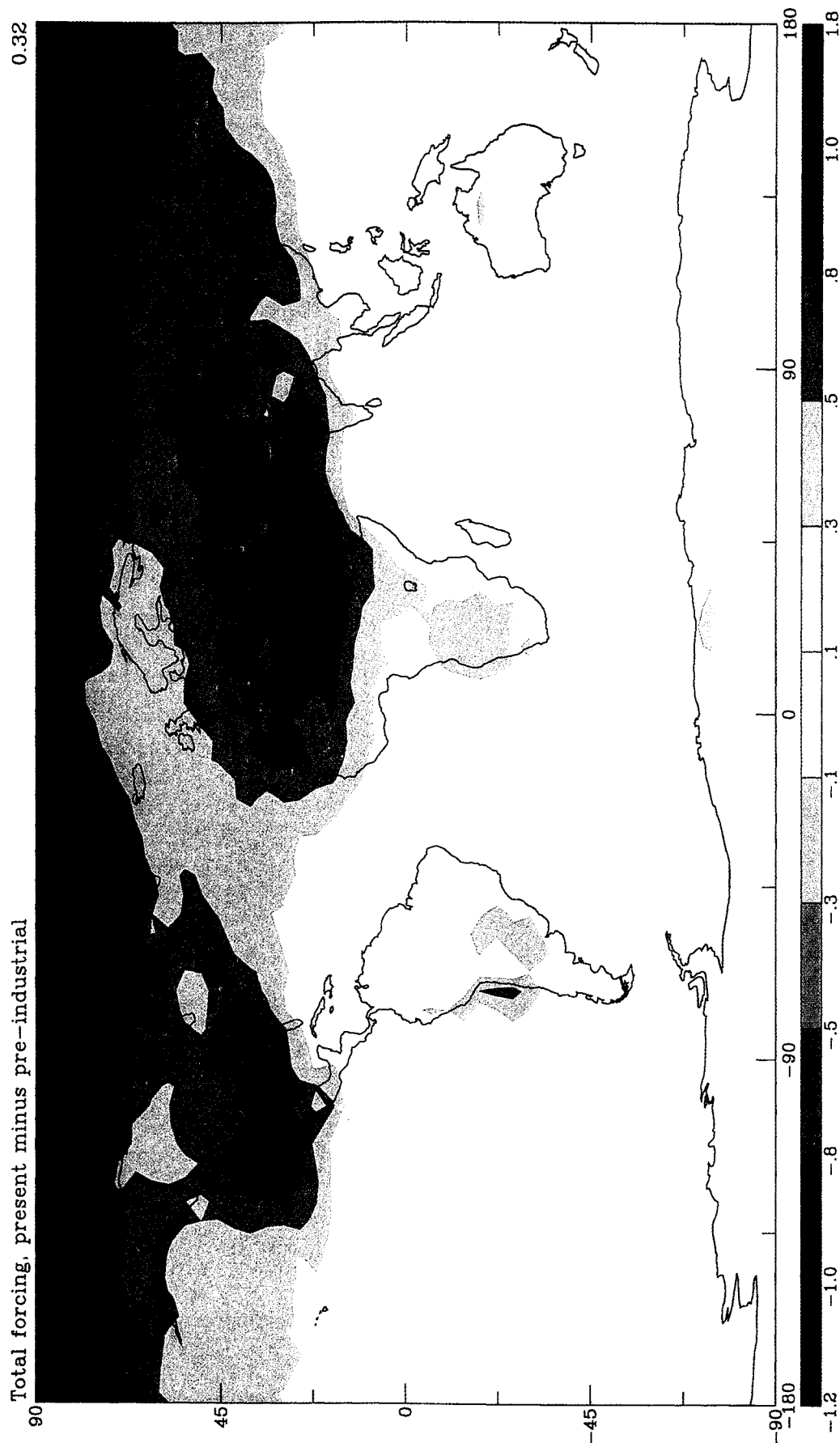
As removal of methane from the atmosphere takes place primarily via oxidation by OH, changes in OH abundances have a large impact on the lifetime of methane. Since methane has contributed the second largest component to the positive

radiative forcing since the preindustrial period, after carbon dioxide [Hansen *et al.*, 1998], it is important to assess how it may have been affected by changing oxidation. Most models find that reduced oxidation capacity has lead to a slower removal of methane emissions from the atmosphere. Brasseur *et al.* [1998] and Stevenson *et al.* [1998] found increases in the methane lifetime of 1.5 and 1.3 years, respectively. Our simulations also show an increase in methane's lifetime since pre-industrial times, but of only 0.4 year, as our oxidation change is less. Note that for the present day we find a total methane oxidation rate of  $492 \text{ Tg yr}^{-1}$ , in good agreement with the recommended value of  $490 \text{ Tg yr}^{-1}$  given in the International Panel on Climate Change [1996].

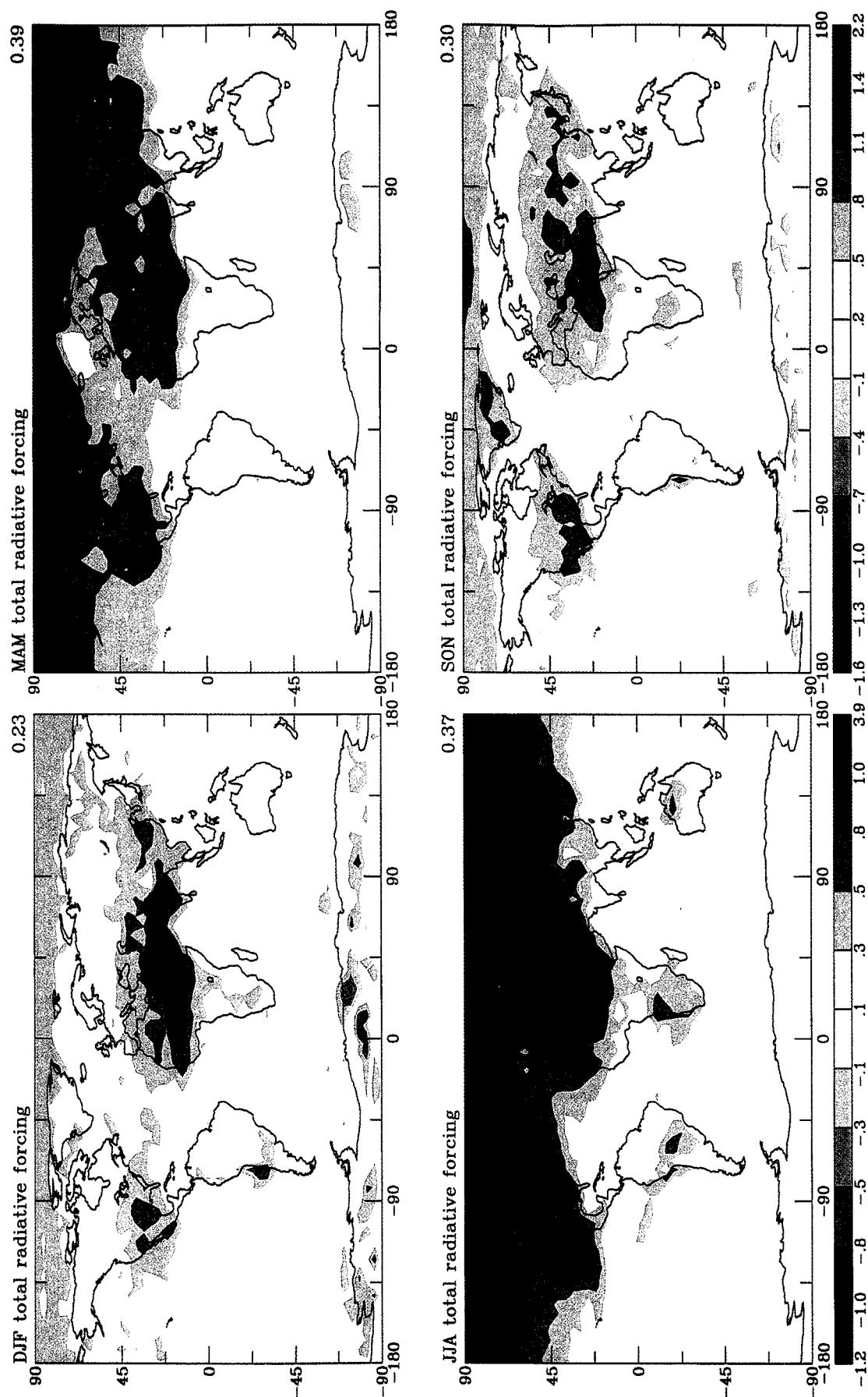
Changes in ozone have resulted primarily from changes in emission of ozone precursors, rather than climate change (see part 2). This is because the abundance of precursors has increased by such a large amount. At Northern Hemisphere mid-latitudes, where the majority of industrialized countries lie, increases in nitrogen oxide abundances have exceeded 1000%, and in carbon monoxide they have exceeded 800%, as shown in Figure 14. These modeled increases are similar in location and magnitude to those shown by Mickley *et al.* [1999]. These changes have dominated the lesser influence of changing temperature and humidity resulting from the increase of greenhouse gases in the atmosphere. We note that the  $\text{NO}_x$  changes include an increase in emissions from lightning of  $0.3 \text{ Tg N}$  (9% of the preindustrial value), which is attributable to climate change rather than anthropogenic emissions.

## 5. Influence of Chemistry-Climate Coupling

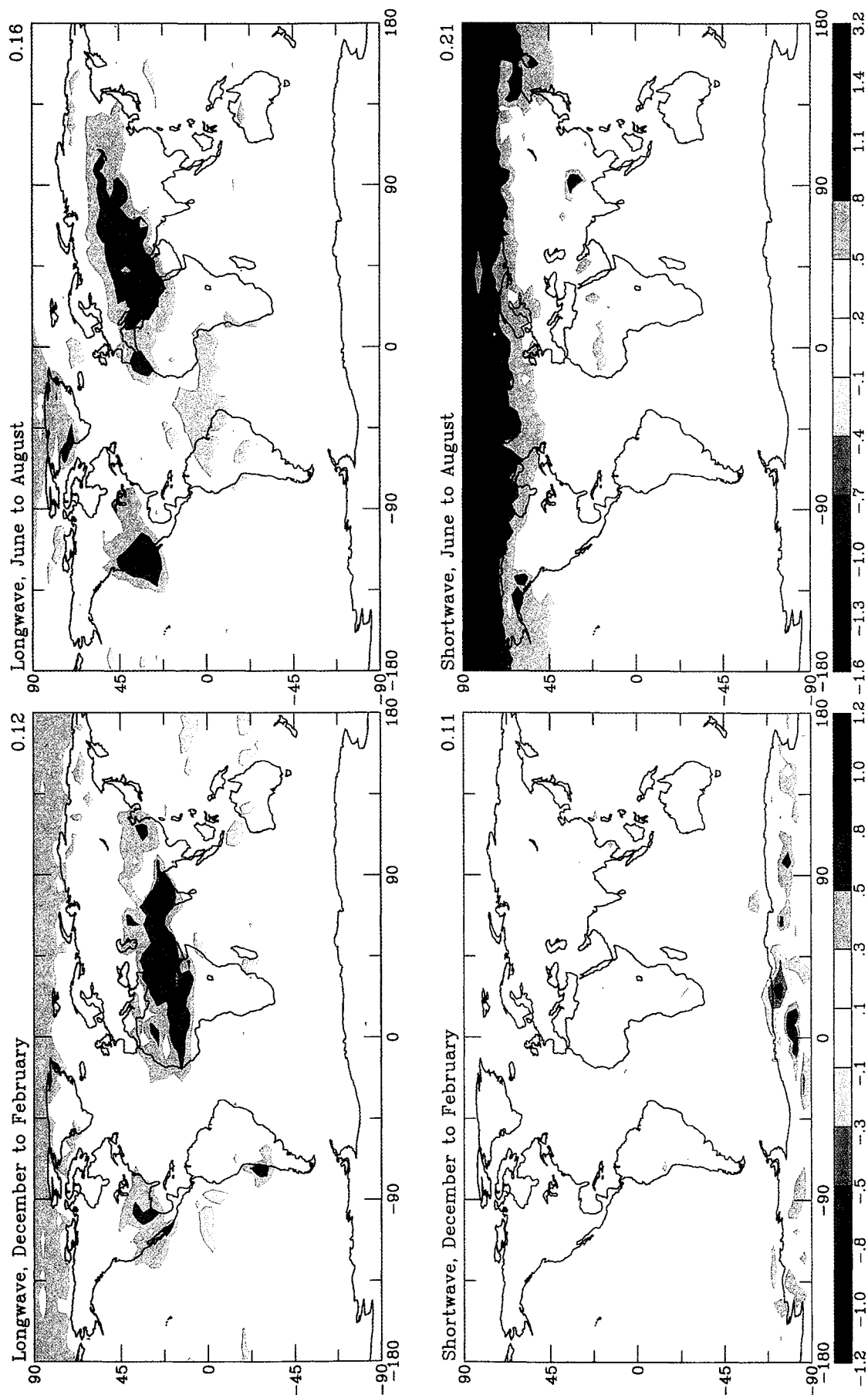
The model has been set up to run with the radiative transfer calculation either responding to the calculated, chemical ozone values (radiatively coupled mode) or using the standard ozone climatology (radiatively uncoupled mode). Comparing the results of the two allows us to discern the influence of the



**Plate 3.** Global mean annual average radiative forcing at the top of the atmosphere due to the tropospheric ozone increase since the preindustrial period ( $\text{W m}^{-2}$ ). The global mean value,  $0.32 \text{ W m}^{-2}$  is shown in the upper right. Results are shown from simulations without ozone feedback onto the GCM's meteorology, though inclusion of this interaction has a small effect on the results (see text).

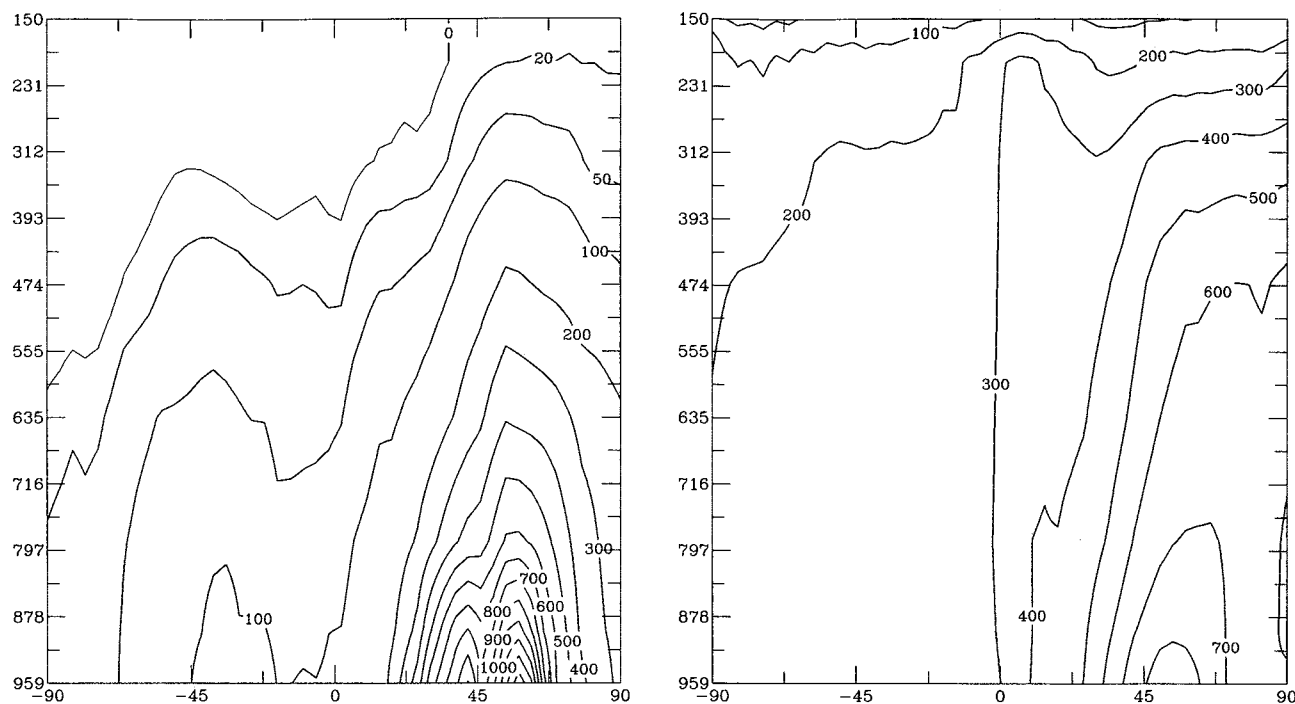


**Plate 4.** Seasonally averaged global mean radiative forcing at the top of the atmosphere due to the tropospheric ozone increase since the preindustrial period ( $\text{W m}^{-2}$ ) from the same runs as in Plate 3. Global mean values are shown in the upper right corner of each plot.



**Plate 5.** (top) Longwave and (bottom) shortwave radiative forcing at the top of the atmosphere due to the tropospheric ozone increase since the preindustrial period (W m<sup>-2</sup>), from the same runs as in Plate 3. Seasonal values are given for (left) December-February and (right) July-August, and global mean values are shown in the upper right corner of each plot.



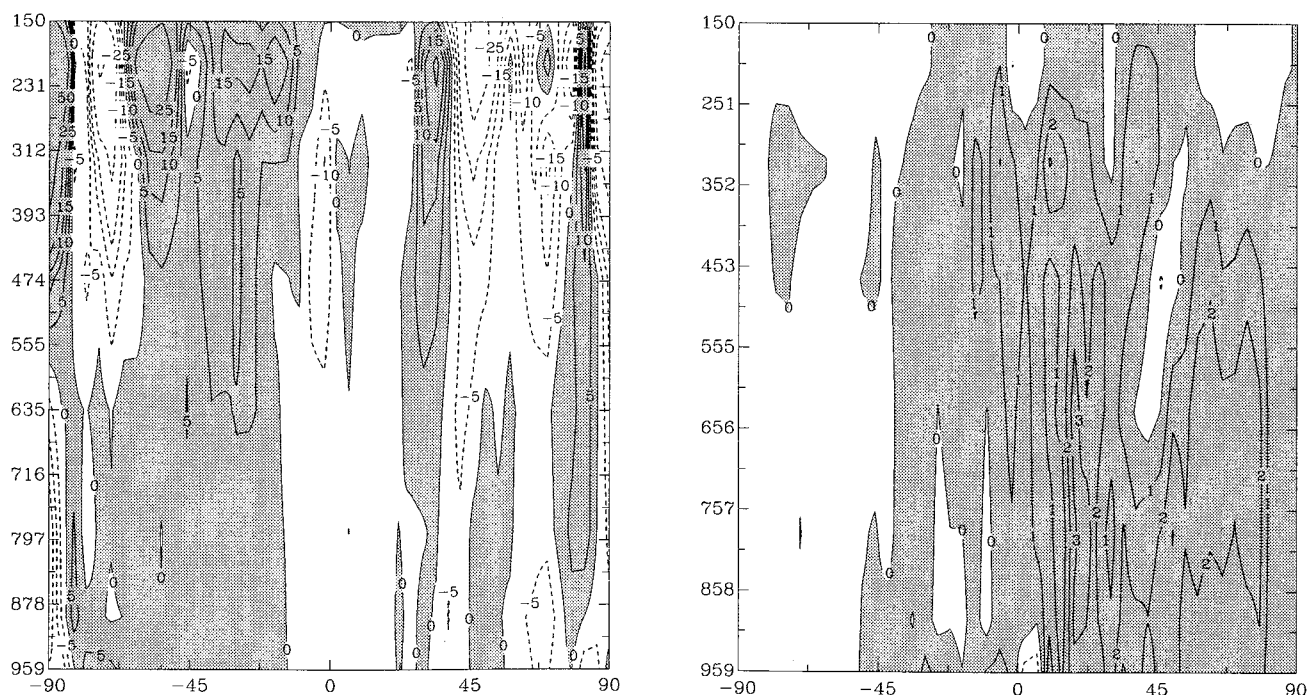


**Figure 14.** (left) Modeled zonal mean change in percent for nitrogen oxides and (right) carbon monoxide from the preindustrial to the present.

coupling between the ozone chemistry and the radiation on the chemistry itself.

The impact is small for the present-day simulation, as climatological ozone values are quite similar to those calculated for current conditions. We find differences in zonal mean ozone of only about  $\pm 2$  ppbv between the coupled and

uncoupled modes. The only statistically significant changes are in the tropical upper troposphere, where the model's ozone values are 1–2 ppbv greater in the radiatively coupled mode. That these differences are quite small is no surprise, however, since the ozone climatology has been created from observations taken during the 1980s.



**Figure 15.** The impact of coupling the calculated ozone to the GCM's radiation and meteorology. Zonal mean differences of the coupled minus the uncoupled modes for (left) ozone (in tenths of ppbv) and (right) hydroxyl (in units of  $10^4$  molecules  $\text{cm}^{-3}$ ) for the preindustrial period.

Of greater interest is how the coupling affects the preindustrial simulation. Figure 15 shows the difference between the coupled and uncoupled modes for zonal mean ozone and hydroxyl during the preindustrial era. Since the climatological values are similar to the present-day calculated values, this difference is also almost identical to the influence of chemistry-radiation coupling on the preindustrial to present-day changes. Since the preindustrial period, ozone values have increased by 20–40 ppbv in much of the Northern Hemisphere, and 1–10 ppbv in much of the Southern Hemisphere, according to the model simulations (as shown in Figure 11). Changing from uncoupled to coupled mode had a minimal effect on the Northern Hemisphere, altering the ozone change by 2% or less (generally reducing the pre-industrial-to-present change), since the huge increase in precursor emissions dominated the overall ozone change. In the Southern Hemisphere the chemistry-radiation coupling played a relatively more important role, accounting for about 3–7% of the increase there. This still represents a small amount of ozone, given that the total increase was less than 10 ppbv. Globally, the chemical-radiative coupling creates only about a tenth of 1% more ozone. We conclude that to a very good approximation the use of online interactively calculated ozone fields is not necessary to properly simulate the ozone distribution for either the current climate or preindustrial conditions, though this may not be true for future conditions.

The results for hydroxyl are more interesting (Figure 15). While changes are small, nearly all the changes in OH from including the chemical-radiative coupling are positive. The decrease in OH from the pre-industrial to the present is therefore enhanced, going from -5.3% in the uncoupled mode to -5.9% in the coupled mode. In our preindustrial simulations the change in tropospheric oxidation capacity is also influenced by reduced sulfate aerosol, greenhouse gases, ocean temperatures and sea ice coverage (see part 2 for further details). As noted in section 4, these factors are commonly neglected but have significant effects. We conclude that while the range of oxidation capacity changes seen in various models is quite large, they may all suffer from systematic biases, in both directions depending on the factors overlooked, in their estimation of the oxidation capacity change over time.

## 6. Radiative Forcing

The global mean annual average radiative forcing at the top of the atmosphere due to the tropospheric ozone increase since the preindustrial period is  $0.32 \text{ W m}^{-2}$  in these simulations. The forcing is predominantly in the Northern Hemisphere, where it is  $0.50 \text{ W m}^{-2}$ , compared with  $0.14 \text{ W m}^{-2}$  in the Southern Hemisphere. The spatial distribution (Plate 3) shows the largest values over the continents at latitudes from around  $15^\circ$  to  $45^\circ\text{N}$  and at high Northern latitudes. This pattern is in general agreement with available results from previous simulations [Berntsen *et al.*, 1997; Stevenson *et al.*, 1998; Haywood *et al.*, 1998].

Radiative forcing was calculated by calling the radiation code twice: once with the climatological ozone values and once with the values calculated by the chemistry routines. This was done for both the preindustrial and the present-day simulations, so that the final values are (present-day flux with calculated ozone minus flux with climatological ozone) minus (preindustrial flux with calculated ozone minus flux with climatological ozone). Though it seems that the climatological ozone term should cancel out, the difference must be taken in each time period to remove the impact of meteorological differences between the two runs. The final forcing thus results solely from the difference between the ozone calculated by the

model's chemistry in each time period. Furthermore, the ozone calculation includes the response to climate change, imposed by increasing greenhouse gas concentrations (affecting temperatures and meteorology) and altered ocean/sea ice boundary conditions. Radiative fluxes are calculated every 5 hours in the GCM. The calculation with the ozone climatology was used to drive the meteorology, which was therefore identical in the two simulations outside of internal variability.

As a test, we also ran the model in the coupled mode, but this made little difference, yielding a forcing of  $0.01 \text{ W m}^{-2}$  larger than that in the uncoupled mode, with most of the increase in the Arctic. (Note that the coupling was incomplete, as the radiative changes were only allowed to affect the atmosphere and land temperatures, and not the sea surface temperatures or sea ice, which may have reduced their impact.) A difficulty in interpreting this result is that the forcing calculation in the coupled mode is inherently an adjusted forcing, not an instantaneous one, since in a fully interactive model, stratospheric temperatures relax to equilibrium following tropospheric ozone perturbations. Adjusted forcing is approximately  $0.02 \text{ W m}^{-2}$  less than the instantaneous forcing for the same perturbation in other models [e.g., Bernsten *et al.*, 1997; Haywood *et al.*, 1998], however. The change from instantaneous to adjusted forcing, while more realistic since the atmosphere is allowed to respond to forcing, may therefore have compensated for this portion of the total change due to the coupling of the calculated ozone to the radiation, which may in fact have increased the radiative forcing by roughly  $0.03 \text{ W m}^{-2}$ , about 10%. That the overall influence of coupling would be positive is consistent with chemical-radiative coupling leading to an overall increase in the ozone burden. Furthermore, the increase is largest in the upper troposphere, where ozone impacts radiative forcing most strongly, suggesting that the 10% increase is probably the more appropriate one.

Seasonal radiative forcing values are largest in Northern Hemisphere spring and summer (Plate 4). Especially large values, greater than  $1.0 \text{ W m}^{-2}$ , are seen during those times over the United States, the Middle East, North Africa, and the Mediterranean, and over large portions of central Asia. The highest values, larger than  $1.5 \text{ W m}^{-2}$ , occur over southern California, northwestern India and Pakistan during spring, central Asia east of the Caspian Sea, and the Arctic. These distributions are overall quite similar to those found using more detailed chemistry in the GISS GCM [Mickley *et al.*, 1999] at most times over most of the globe. The summer maxima described above match extremely well with the more complex model. Primary exceptions are the southern Atlantic during September–November, when the forcing is larger in the Mickley *et al.* model, and the Arctic during March–May, when the forcing is much smaller in the other model. The former difference is likely related to a reduced influence of biomass burning in this region due to an  $\text{NO}_x$  biomass burning source more than 50% smaller than that used by Mickley *et al.* [1999] (the actual value is quite uncertain), and perhaps also to the lack of burning emissions of higher hydrocarbons. A clue to the Arctic differences can be gained by examining the shortwave and longwave components separately. The December–February (DJF) and July–August (JJA) values are shown in Plate 5. The very large forcing values seen in this model over the Arctic result predominantly from changes in the shortwave. This is expected, as the high ice albedo over Greenland and the Arctic is very effective at reflecting sunlight, which can then be absorbed by the additional ozone. While shortwave forcing also maximizes over the Arctic during JJA in the more complex model of Mickley *et al.*, the forcing is not quite as large as that shown here. The same bias likely affects the March–May results even more strongly. Figure 1 showed that the simulations

overestimated the amount of ozone at Resolute (75°N) in the lower troposphere from around 500 to 800 mbar (carbon monoxide values were also overestimated in the Arctic, as shown in Figure 4). Since even small amounts of ozone can have a large effect on the forcing in the shortwave, this bias is probably responsible for most of the large forcing values in the Arctic during sunlit periods. However, the model underestimated ozone in the lower stratosphere at 200 mbar, which might have been expected to contribute even more strongly to reducing the radiative forcing. Figure 1 also showed that the model did a fairly good job of reproducing ozone values outside the Arctic, in accord with its ability to reproduce the more complex model's radiative forcing values across most of the rest of the globe quite well.

Our calculated global annual average radiative forcing from anthropogenic ozone of  $0.32 \text{ W m}^{-2}$  lies within the range of  $0.28 - 0.55 \text{ W m}^{-2}$  found in other three-dimensional global models [Hauglustaine *et al.*, 1994; Roelofs *et al.*, 1997; van Dorland *et al.*, 1997; Berntsen *et al.*, 1997; Stevenson *et al.*, 1998; Haywood *et al.*, 1998; Brasseur *et al.*, 1998; Kiehl *et al.*, 1999; Mickley *et al.*, 1999; Lelieveld and Dentener, 2000]. It is similar to, though somewhat less than, the  $0.44 \text{ W m}^{-2}$  found in the Mickley *et al.* [1999] model. The values are especially similar in the Northern Hemisphere ( $0.50 \text{ W m}^{-2}$  versus  $0.53 \text{ W m}^{-2}$ ), while the discrepancy arises primarily from the lower value seen in our model in the Southern Hemisphere ( $0.14 \text{ W m}^{-2}$  versus  $0.34 \text{ W m}^{-2}$ ). This is partially due to the much larger  $\text{NO}_x$  biomass burning source used in the Mickley *et al.* [1999] study. Additionally, Mickley *et al.* reduced the emissions of  $\text{NO}_x$  from soils in the pre-industrial, and we did not. These differences in  $\text{NO}_x$  take on a greater importance in the less polluted Southern Hemisphere. Furthermore, the small amount of radiative forcing seen in the Southern Hemisphere is strongly influenced by the retreat of sea ice around Antarctica from the preindustrial to the present (see Figure 10). As greenhouse gases build up in the atmosphere, the resulting global warming affects surface temperatures globally. Where sea ice is present, however, there is an additional ice-albedo feedback on warming, since warmer temperatures melt ice, reducing the surface albedo, hence further warming the surface (this feedback is not included in these chemistry runs with prescribed ocean/ice conditions but was included in the original simulations that derived the conditions used here). This is seen most strongly at the Antarctic sea ice margin in the model, where small temperature changes can have a large effect as the temperatures are near the threshold for formation and maintenance of sea ice. The decreased albedo resulting from the sea-ice retreat compensates for a large fraction of the increase of ozone in the Southern Hemisphere. While the greater ozone abundance in the present day increases the radiative forcing, the reduced shortwave reflectivity of the surface reduces the forcing per unit ozone. One need only look at the very large shortwave forcing values found over the Arctic (Plate 5) to see the importance of the high albedo (discussed above). While the shortwave forcing during Northern Hemisphere summer is greater than  $1.5 \text{ W m}^{-2}$  over a large portion of the Arctic, it is only about  $0.1 \text{ W m}^{-2}$  over a similar sized area of the Antarctic during the southern summer (Plate 5). This is a far greater relative difference than that seen in ozone, which increased by about 5 ppbv over the Antarctic sea ice margin and by about 30 ppbv over the Arctic sea ice margin.

Overall, the radiative forcing in the Southern Hemisphere is smaller in this model due to several factors. The primary influences are the different biomass burning and soil sources of  $\text{NO}_x$ , a greater amount of sea ice around Antarctica in the preindustrial era, and the smaller overall change in total ozone. Our increase in the ozone burden was 82 Tg, as compared with 130 Tg by Mickley *et al.* [1999].

## 7. Discussion/Conclusions

We have developed a simplified, fast tropospheric chemistry model which runs interactively within the GISS climate model. The model is largely able to reproduce observed ozone vertical profiles and annual cycles, despite the relatively simple chemistry scheme used. The lack of non-methane hydrocarbon chemistry in the model does not seem to greatly affect the quality of the simulated ozone field, in accord with other modeling studies [e.g., Wang *et al.*, 1998c]. The model also calculates radiative forcing values due to anthropogenic ozone that are quite similar to those seen in other, more complex models. This is not surprising, given that the model does a good job with the ozone distribution itself. However, though most of the chemical transport models or coupled chemistry-climate GCMs also reproduce these observations, there remain significant differences in the ozone budgets of the various models. The large range of ozone budget terms that seem able to yield ozone values in agreement with measurements indicates that large uncertainties persist in understanding the relative importance of the various factors governing tropospheric ozone abundances.

The model has been compared extensively throughout this paper with the results from a more detailed chemistry module which has also been used within the GISS GCM [Mickley *et al.*, 1999]. Though the models use the same basic GCM, so that the dynamics and meteorology are calculated identically, there are several differences besides the chemical schemes. This model uses a somewhat newer version of the GCM, with several improvements to the convection scheme amongst other changes. In these simulations we also allowed the model to calculate transport from the stratosphere to the troposphere, while this was prescribed in the Mickley *et al.* [1999] work. This study also assumed a smaller present-day biomass burning source of nitrogen oxides, and kept  $\text{NO}_x$  from soils constant over time. For the preindustrial period we included altered sulfate and ocean surface conditions, which were kept at present-day values in the simulation of Mickley *et al.* [1999]. Nevertheless, for quantities which are lacking in observations, comparison with the more detailed model has provided an important test of the validity of using a simplified chemistry scheme for climate studies.

In general, the simplified chemistry model performs quite well. Noticeable differences include present-day ozone over the South Atlantic during fall, where the Mickley *et al.* [1999] model has larger ozone amounts, likely as a result of greater emissions from biomass burning. Given that both models have difficulties in matching observations of hydrogen peroxide or nitrogen species in this area, it is not obvious which is performing better. Another difference is reduced Southern Hemisphere radiative forcing from anthropogenic ozone, which we attribute largely to the Antarctic sea ice changes imposed on the model. It also appears that our model had greater difficulty with stratosphere-troposphere exchange. This is especially evident in the Arctic, where the current work overestimates ozone abundances. We hope to improve the representation of the exchange process in future versions, tests of which have already shown considerable advances. Overall, the contribution of chemistry to the ozone budget was quite similar in the two models (370 Tg  $\text{yr}^{-1}$  in Mickley *et al.* versus 389 Tg  $\text{yr}^{-1}$  in this work, out of a range of  $-810 \text{ Tg yr}^{-1}$  to  $+550 \text{ Tg yr}^{-1}$  in other models), and the overall ozone distributions were also fairly similar.

The calculated radiative forcing is most important for climate studies. The model calculates a radiative forcing from tropospheric ozone between the preindustrial and the present of  $0.32 \text{ W m}^{-2}$ . We find that coupling the calculated ozone to the GCM's radiation, and hence, to the meteorology, has a fairly

small impact. It increases the radiative forcing by about 3%, though since this is an adjusted forcing, which is typically about 6% less than an instantaneous forcing (the 0.32 W m<sup>-2</sup> value found in the uncoupled mode), coupling the ozone to the radiation has likely increased the radiative forcing by approximately 10% (0.03 W m<sup>-2</sup>). In general, the distribution and magnitude of the radiative forcing due to preindustrial to present-day ozone increases matched quite well with the more detailed model of Mickley *et al.* [1999] and is similar to other models as well. Therefore we believe that this coupled chemistry-climate model can be used for realistic climate studies. Since it uses simplified chemistry, and therefore runs quite rapidly, it is ideally suited to study issues such as the relative importance of individual aspects of chemistry-climate interactions over time (e.g., changes in greenhouse gases, ocean temperatures and sea ice coverage, individual emission sources, lightning, etc.), which require many simulations.

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